PB 190 170

MATHEMATICAL MODEL OF TERTIARY TREATMENT BY LIME ADDITION

L. Seiden, et al

General American Transportation Corporation
Niles, Illinois

September 1969

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ROBERT A. TAFT WATER RESEARCH CENTER
REPORT NO. TWRC-14

PB190170

MATHEMATICAL MODEL OF TERTIARY TREATMENT BY LIME ADDITION

ADVANCED WASTE TREATMENT RESEARCH LABORATORY— XIV

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Cincinnati, Ohio

80

1 Accession Number	2 Subject Field & Group	SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM
W70-04547	05D	

5 Organization

General American Corporation, Research Division.

6 Title

MATHEMATICAL MODEL OF TERTIARY TREATMENT BY LIME ADDITION,

10 Author(s)

Seiden, L. and
Patel, K.

16 Project Designation

Contract No 14-12-416 FWPCA Project 17010---9/69

21 ~~Request for report should be sent to Office of Information, Federal Water Pollution Control Admin, 4676 Columbia Parkway, Cincinnati, Ohio 45226.~~

21

Available from the Clearinghouse as PB , $3 in paper copy, 65¢ in microfiche

PB 190 170

22 Citation

Robert A. Taft Water Research Center Report No TWRC-14, Federal Water Pollution Control Administration, September 1969. 69 p, 10 fig, 5 tab, 152 ref, 3 append.

23 Descriptors (Starred First)

*Mathematical models, *Tertiary treatment, *Lime, *Phosphorus compounds, *Computer programs, Effluents, Acidity, Cost analysis, Streams, Streamflow, Flow rates, Coagulation.

25 Identifiers (Starred First)

Secondary effluents, *Phosphorus removal.

27 Abstract

The status of phosphorus removal from secondary effluents by lime addition is presented. Based on the empirical information available, a mathematical model of the process was developed. The factor which best correlated with phosphorus removal was the pH of the tertiary effluent. Cost information for the model was generated based on a solids-contact type precipitator such as the Infilco Densator. A computer program, in FORTRAN IV, derived from the model, was developed for use as a subroutine in the FWPCA Executive Calling Program. Given the input stream flow rate and analyses, and the final pH, the program computes the necessary doses of lime and coagulant, their costs, the size and cost of the equipment, the degree of phosphorus removal, and the output stream analyses.

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WR:102 (REV. JULY 1969)
WRSIC

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MATHEMATICAL MODEL OF TERTIARY TREATMENT
BY
LIME ADDITION

by

L. Seiden and K. Patel

for

The Advanced Waste Treatment Research Laboratory

Robert A. Taft Water Research Center

This report is submitted in fulfillment of Contract No. 14-12-416 between the Federal Water Pollution Control Administration and General American Research Division.

U. S. Department of the Interior
Federal Water Pollution Control Administration
Cincinnati, Ohio

September 1969

FOREWORD

In its assigned function as the Nation's principal natural resource agency, the United States Department of the Interior bears a special obligation to ensure that our expendable resources are conserved, and that all resources contribute their full measure to the progress, prosperity, and security of America -- now and in the future.

This series of reports has been established to present the results of intramural and contract research studies carried out under the guidance of the technical staff of the FWPCA Robert A. Taft Water Research Center for the purpose of developing new or improved wastewater treatment methods. Included is work conducted under cooperative and contractual agreements with Federal, state, and local agencies, research institutions, and industrial organizations. The reports are published essentially as submitted by the investigators. The ideas and conclusions presented are, therefore, those of the investigators and not necessarily those of the FWPCA.

ACKNOWLEDGEMENT

This program was performed for FWPCA under Contract No. 14-12-416. The Project Officer was Mr. Robert Smith, Chief, Treatment Optimization Research Program, Advanced Waste Treatment Research Laboratory.

The authors wish to thank Messrs. Dolloff F. Bishop, Chief, FWPCA-DC Pilot Plant, and Edward L. Berg, Municipal Treatment Research Program, Advanced Waste Treatment Research Laboratory, FWPCA, for kindly supplying us with information relative to their operating experience at Blue Plains, D. C. and Lebanon, Ohio, respectively, and for their cooperation during our visits to these installations. We also wish to express thanks to Mr. James Zornes, Production Manager, Nevada Power Company.

In addition we wish to acknowledge the assistance of Mr. Joseph F. Roesler, Advanced Waste Treatment Research Laboratory, FWPCA, for his interest and helpful comments during the course of this project.

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ABSTRACT

The status of phosphorus removal from secondary effluents by lime addition is presented. Based on the empirical information available, a mathematical model of the process was developed.

The factor which best correlated with phosphorus removal was the pH of the tertiary effluent. Cost information for the model was generated based on a solids-contact type precipitator such as the Infilco Densator.

A computer program, in FORTRAN IV, derived from the model, was developed for use as a subroutine in the FWPCA Executive Calling Program. Given the input stream flow rate and analyses, and the final pH, the program computes the necessary doses of lime and coagulant, their costs, the size and cost of the equipment, the degree of phosphorus removal, and the output stream analyses.

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INTRODUCTION

During the past decade, there has been a growing public awareness of the necessity for more diligently conserving our water resources. The growth of urbanization and industrialization have placed increasingly heavier loads on what were at one time considered adequate waste-water treatment facilities and processes. It is now quite clear that, if the quality of our environment is to be maintained, prompt attention must be given to the development and application of more advanced and rigorous waste-water treatment techniques.

Excluding gross chemical pollution by specialized industries, which may be dealt with on an individual basis, a problem common to almost all municipal waste-treatment facilities is that of nutrient removal. It is now well established that even moderately high levels of phosphorus and/or nitrogen in sewage plant effluents accelerate the rate of eutrophication in receiving waters and serve as nutrient material for undesirable algal blooms. With phosphorus in particular, this problem has been aggravated by the growing use of phosphorus-containing detergents.

Thus, P removal is one of several high-priority "advanced" waste-treatment process which are being investigated by the Federal Water Pollution Control Administration.

Reduction of phosphorus levels in sewage plant effluents may be accomplished by several means. The purpose of this report is to describe one method in particular: chemical precipitation by lime addition as a tertiary treatment process, i.e., one which follows the well-established primary and secondary (activated sludge) treatment steps.

P removal by lime addition is accomplished via the precipitation of calcium phosphate. It is known that a relatively high pH is necessary for this to occur, and the reaction: $CaO + H_2O \rightarrow Ca^{2+} + 2OH^-$ accomplishes this. The resultant high pH of the effluent also makes the process desirable as it converts nitrogen in the form of NH_4^+ ion into NH_3, allowing a subsequent ammonia-stripping step (removal of another possible nutrient, nitrogen) with no further pH adjustment.

The objectives of this project, sponsored by the FWPCA, were to survey the current status of the process, to attempt a mathematical modeling of the process, and to develop a computer program for describing the performance and cost relationships involved. The computer program is meant to be used as a subroutine for the Executive Calling Program being developed by the Operations Research Unit of FWPCA.

Because of the association of General American Research Division with Infilco/Fuller Corporation, it was requested that the modeling of the process be in terms of solids-contact type precipitation equipment such as the Infilco Densator.

DESCRIPTION OF THE TERTIARY LIME TREATMENT PROCESS

Any attempt to describe or model the process in question must recognize that it in reality consists of at least two groups of sub-processes. We have first the chemical reactions which occur when lime is added to a phosphate-bearing secondary effluent. This is followed by the physical (or physico-chemical) processes involved in coagulation, flocculation, and sedimentation of the solids formed by the chemical reactions. This division into discrete "steps" is somewhat arbitrary, as there is undoubtedly much interaction of one upon the other; it is, however, convenient for the purposes of exposition.

CHEMICAL REACTIONS

$CaCO_3$ and $Mg(OH)_2$ Precipitation

The addition of lime (either quicklime, CaO, or slaked lime, $Ca(OH)_2$) to a secondary effluent will, in addition to the precipitation of phosphate, result in the formation of a relatively large amount of solid calcium carbonate. This is identical to the standard cold-lime softening process, in which CO_2 and HCO_3^- react, as the pH increases, to form CO_3^{2-}, which in turn precipitates insoluble $CaCO_3$.

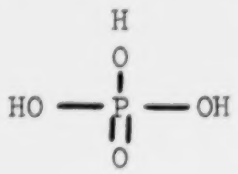
With increasing lime dose (and pH), any magnesium present in the system will also begin to precipitate as $Mg(OH)_2$. This usually occurs at pH's in the vicinity of 11.0.

Precipitation of Phosphates

Phosphorus Chemistry

Before discussing the interaction of lime with phosphates, it might be well to briefly describe and define some aspects of the chemistry of phosphates.

We may first define "ortho-phosphates" as those phosphorus-containing compounds or ions which are derived from orthophosphoric acid, H_3PO_4:



This compound in solution will lose from one to all three of its protons, yielding the orthophosphate ions $H_2PO_4^-$, HPO_4^{2-}, or PO_4^{3-}, thus:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^{3-}$$
$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$$
$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$$

The particular ionic forms in which orthophosphate exists is determined by the hydrogen ion activity of the solution (approximately equal to the H^+ concentration), according to the relations:

$$\frac{[H_2PO_4^-][H^+]}{[H_3PO_4]} = K_1 \approx 7.10 \times 10^{-3} \quad (1)$$

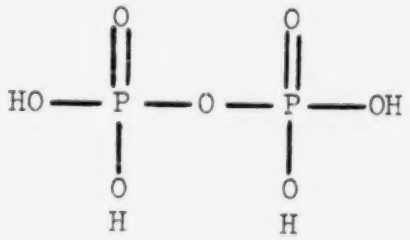
$$\frac{[HPO_4^{2-}][H^+]}{[H_2PO_4^-]} = K_2 \approx 7.99 \times 10^{-8} \quad (2)$$

$$\frac{[PO_4^{3-}][H^+]}{[HPO_4^{2-}]} = K_3 \approx 4.8 \times 10^{-13} \quad (3)$$

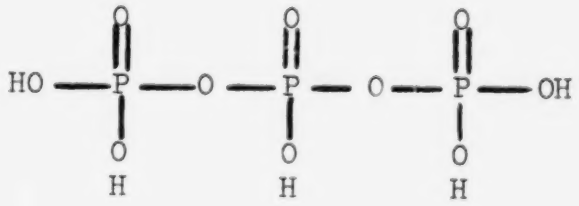
where the brackets denote molar activities and K_1, K_2 and K_3 are the constants at 25°C. Figure 1 shows the relative amounts of each species which are present in the pH range from 8-12. Over most of this range, HPO_4^{2-} is by far the dominant form.

So-called "poly" or "condensed" phosphates are derived from phosphoric acid species which contain two or more phosphorus atoms, alinked through an oxygen bridge, e.g.:

Pyrophosphoric acid:



Tripolyphosphoric acid:



In a similar manner, these acids may lose protons, resulting in ions of various charge. These condensed phosphates may either be in the form of chains, as above, or in rings.

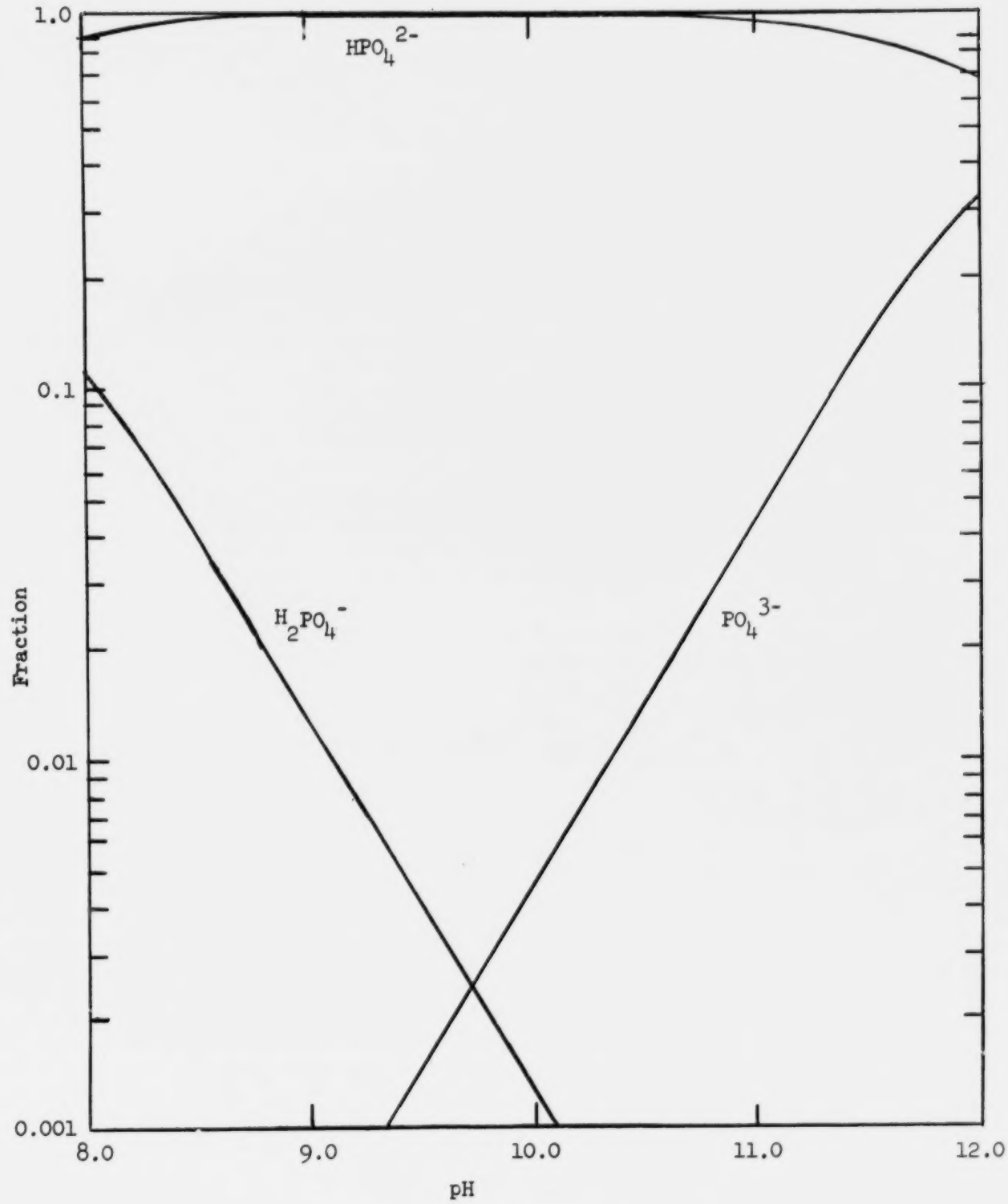


FIGURE 1. Fraction of Orthophosphate in Each Form vs. pH

The condensed phosphate ions, in general, do not form particularly insoluble salts with calcium, although some do combine with Ca^{2+} ions to form soluble complexes.

In a well-stabilized secondary effluent, condensed phosphates normally constitute no more than 10% of the total phosphate present.

Reaction with Lime

The chemical interactions which occur when lime is added to a secondary waste-water containing phosphorus compounds are quite complex and not fully understood. This is not surprising, in that even the chemistry of a "pure" aqueous system, containing only calcium and ortho-phosphate ions, is not readily susceptible to simple analysis in terms of classical chemical concepts of solubility products, etc. Indeed, the calcium-phosphate precipitate formed may vary in composition depending on the conditions of formation, such as temperature, pH, Ca/P ratio in the precipitating solution, and other unknown factors. The calcium orthophosphate precipitate has the basic structure of a hydroxyapatite, and is usually considered to be $Ca_{10}(OH)_2(PO_4)_6$. However, the Ca/P atomic ratios in the solid material are found to vary from 1.33 to 2.0.(1)

The apparent solubility product constant of this material,

$$K_{SP} = (Ca)^{10} (PO_4)^6 (OH)^2 \qquad (4)$$

as measured by several workers, shows a variation over a range of 10^{11}. Clark(2) has recently carefully measured this product to be 10^{-115}. Using this criterion, it can be shown that a moderately hard typical secondary effluent containing approximately 50 mg/l Ca, 10 mg/l PO_4, and at a pH of about 8, should need no further treatment for phosphorus removal, the maximum "equilibrium" ortho-phosphate concentration being about 10^{-3} mg/l PO_4. As this is obviously not the case, it appears that a solubility product-type calculation is inappropriate for predicting P removal. The possible reasons for the deviation of this system from "ideal" behavior are many, and will not be dealt with in detail. Among them are: (a) sluggishness of the precipitation process, including formation of colloidal particles which will not settle out or be caught by filters; (b) inhibition of or interference with the reaction due to the presence of other soluble species, particularly organics.

Going from the "pure water" case to a more realistic one, we must take into account the presence of Mg^{2+}, CO_3^{2-}, and HCO_3^- ions, solid $Mg(OH)_2$ and $CaCO_3$, and the presence of a small but significant amount of condensed phosphates. This increases even further the complexity of trying to deal with phosphorus removal according to classical theoretical concepts. These species

---

(1) References are listed in Appendix B.

will all interact with each other; the presence of solid $CaCO_3$ and $Mg(OH)_2$ may result in more efficient precipitation of calcium phosphate by decreasing the tendency for self-nucleation and colloid formation. The presence of polyphosphates, on the other hand, is known to inhibit the precipitation of calcium carbonate. $Mg(OH)_2$ in particular is said to enhance P-removal by acting as a flocculating agent. Schmid(3) has demonstrated that polyphosphate is removed from solution to a large extent by adsorption on both $Ca\text{-}PO_4$ and $CaCO_3$ sludge particles.

PHYSICAL PROCESSES

If a solution is supersaturated with respect to a particular solid species, this supersaturation may be relieved in one of two ways: (a) by deposition of solid material onto the surfaces of previously formed precipitate particles, or (b) by spontaneous self-nucleation, i.e., the formation of many small crystal nuclei. This latter process is undesirable in that it leads to the presence of a large number of very small (colloidal) particles which do not settle, and may not be filterable. Usually this phenomenon occurs at high degrees of supersaturation.

The chemical reactions in the preceding section have been described as if they proceeded instantaneously. In reality, a finite time is involved in the formation and growth of precipitate particles. In general, the rate of a precipitation process is proportional to both the degree of supersaturation and the surface area available for further crystallization.

The aims in the process being considered are, of course, to have the precipitation reactions occur as rapidly as possible, yet with the least degree of self-nucleation. The design of a solids-contact type precipitator, such as a Densator, is meant to accomplish both of these aims. It does this by recirculating a relatively high concentration of previously formed sludge into the reaction zone where lime is being added to the influent stream. A high degree of agitation is provided here, for good mixing. In this manner, a large surface area for new precipitation is supplied, increasing the rate of solids formation and decreasing the tendency for spontaneous nucleation. Figure 2 shows a typical Densator configuration.

After passing through the "primary" reaction zone where lime and recycle sludge are added, the influent stream then passes down through a "secondary" reaction zone. Here the degree of agitation is more gentle, and coagulation and flocculation occur, leading to particle size growth by particle-particle collision and agglomeration. (There is provision here for so-called "split-stream" treatment, where only a portion of the influent stream is supplied to the primary zone, the balance entering in the secondary zone. While desirable for softening applications, it is not clear whether there is any advantage in using this split-stream technique in tertiary treatment.) It is here that coagulants may be introduced, if needed.

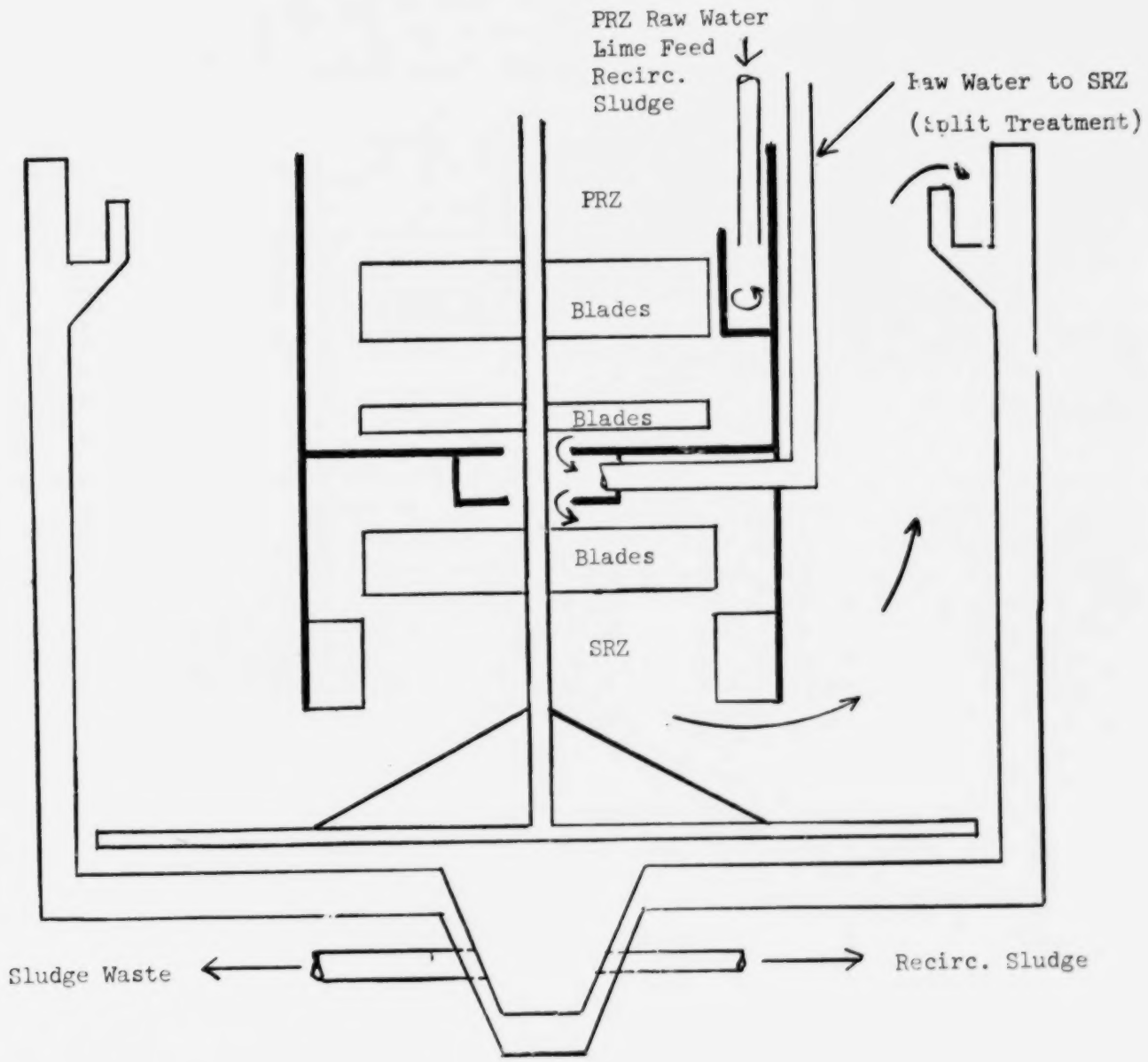


FIGURE 2. Typical Densator Configuration

Upon exiting the secondary zone, the stream then turns upward into the external clarification or sedimentation region. Here again, there is more opportunity for particle-particle interaction and growth. The solids settle to the bottom of the unit, while the clarified water is drawn off the top.

From the above description of the "physical" processes, the complexity of the situation may be appreciated. Even assuming one knows precisely the amounts of chemical solids formed, one must then be able to relate the degree of clarification to the physical parameters of the system such as sludge recycle rate, flocculation and sedimentation zone residence times, agitation velocities, upflow rates, etc.

It is apparent how the chemical and physical processes may interact with each other. Thus, the physical parameters such as recycle sludge concentration affect the chemistry by determining the rates of formation of precipitates. At the same time, the chemistry of the system, such as the amount of $Mg(OH)_2$ formed (which acts as a coagulant), will affect the physical processes of coagulation, flocculation and sedimentation.

LITERATURE SURVEY

As a preliminary effort, a literature survey was made to determine the state-of-the-art of phosphorus removal from secondary effluents by chemical treatment.

There are three basic techniques which have been studied in any detail. These include the addition of lime, alum, and iron salts. While all of these have long been recognized for their usefulness in clarification of waste waters, it has been only relatively recently that workers have looked at their effectiveness for P removal. This work, the bulk of which dates from the late 1940's and early 1950's, has been directed not only at P removal in a discrete tertiary step, but also by chemical additions in earlier phases of the conventional treatment processes. We have, however, concentrated primarily on those articles which would be applicable in the context of a chemical precipitation process following conventional secondary treatment.

CHEMICAL PRECIPITATIONS

The work of Sawyer[4] and Owen[5] established the efficacy of lime, alum, and iron salts in removing phosphorus from secondary effluents. Sawyer worked with all three, and his results indicated that the dose needed for a given P removal with alum or $FeCl_3$ was increased when polyphosphates were added to the system, but that the lime requirement was not increased. Lea, Rohlich and Katz[6] investigated aluminum sulfate, ferric and ferrous sulfate, and copper sulfate, and concluded that of these, filter alum was the most suitable coagulant for phosphorus removal, because of the possibility of coagulant recovery. They also concluded that the P-removal mechanism with these chemicals was primarily via adsorption on the hydroxide flocs formed, with possibly some precipitation of ferrous phosphate as well.

Henriksen[7] studied the coagulation of P by iron and aluminum salts, and found that for a given P removal, the necessary doses were dependent on the initial P concentration. These findings were borne out for alum by Malhotra, Lee and Rohlich[8], who also concluded that on a chemical cost basis, lime would be the most economical chemical precipitant for the activated sludge effluent at Madison, Wisconsin. Their prime objection to the use of lime was the high pH of the resulting effluent. (This, of course, would not be objectionable if a subsequent ammonia removal step were contemplated.)

Culp[9] has reported on the waste-water reclamation plant at South Tahoe, California, where alum addition, followed by filtration and final polishing, was used for P removal in a 2.5 mgd tertiary plant. Studies conducted during construction and initial operation showed that the initially contemplated alkaline recovery of the alum would not be feasible, and the plant has now gone over to lime addition.

LIME ADDITION

Owen[5] performed both laboratory and field studies of lime addition to a secondary effluent. His laboratory results indicated that by dosing with lime to a pH of 11.0, essentially complete removal of phosphorus could be achieved. These studies also pointed out the importance of good solids removal. Samples settled for one hour yielded P concentrations of 0.3 mg/l, while in those settled for 18 hours, the residual P concentration was 0.015 mg/l. His field tests were performed on the effluent from a trickling filter secondary system; with admittedly crude mixing and dosing equipment, he achieved soluble phosphorus residuals of 0.13 ppm with a dose of 720 ppm $Ca(OH)_2$ (equivalent to 520 ppm CaO).

Rudolfs[10], in studies directed primarily at clarification rather than P removal, showed that addition of Ca alone did not result in appreciable precipitation of phosphorus, whereas subsequently raising the pH with NaOH decreased the P content of the solutions. More recently, Malhotra[11] obtained similar results, reporting on jar tests with secondary effluents in which P removals of 92-96% were obtained (with an initial Ca concentration of 63 mg/l) by adding NaOH to obtain a pH of 11.5.

Schmid[3] performed a large number of jar tests on synthetic sewage effluents in order to determine the relations and interactions between Ca^{2+}, CO_3^{2-}, ortho-phosphates, and polyphosphates in the precipitation reactions. The context of this study was in terms of a combined lime-biological treatment system for raw sewage rather than tertiary treatment; therefore, many of the experiments were run with higher orthophosphates and polyphosphate concentrations, and at lower pH's, than would be typical of a tertiary process. However, a good deal of this work is of interest in elucidating the mechanism of phosphate removal. Among his finds were: (a) at pH's higher than 9, polyphosphates are removed from solution primarily by adsorption on calcium carbonate and calcium orthophosphate precipitates; (b) the presence of polyphosphates results in marked inhibition of $CaCO_3$ precipitation (at least at pH's up to 10.5); (c) while the presence of $CaCO_3$ precipitate is not necessary for the precipitation of orthophosphate, it appears to be required for efficient removal of polyphosphates (probably because it provides the necessary adsorption surface).

In addition to the documents cited above, many more were surveyed, including those pertaining not only to the chemistry of the process, but also to the physical aspects of coagulation, flocculation and sedimentation. As with the above papers, most were found to be useful in terms of general background information, but of little quantitative value in attempting to model the actual performance of the P removal process. It was, therefore, not considered appropriate to include them in the body of this report. A reading list covering most of these documents will be found in Appendix C, where they are classified according to primary subject matter.

SURVEY OF OPERATING PLANTS AND PILOT PLANTS

Weinberger[12] has listed those plants or pilot plants which have operational experience with tertiary phosphorus removal by lime addition, or which are doing research on this topic. These include those at South Tahoe, California, Washington, D. C., and Las Vegas, Nevada. In addition, pilot plant units at Lebanon, Ohio, and Pomona, California have also done some work in this respect.

A great hindrance to the modeling process has been the scarcity of reliable, pertinent data which is available from these sources. It is helpful, in a project of this sort, to have a large amount of data, taken at many different installations and taken under many different operating conditions, so as to be able to obtain correlations which would be of general applicability in predicting performance.

Unfortunately, such has not been the case in this study. Except in certain limited cases, it has not been possible, when studying the effects of one variable, to ensure that other possible variables are remaining fixed. In many cases, information concerning possible parameters of interest has not been available. Thus, for example, effluent phosphorus analyses have sometimes been supplied with no distinction between condensed and ortho, or filtered and unfiltered. Little information concerning influent analyses has been available. Those plants obtaining satisfactory effluent quality for their particular application have done little in the way of varying their operation parameters. In several plants, phosphorus removal has been a secondary consideration to some other goals. Thus, the population from which our correlations have been drawn has been an extremely limited one. As will be explained in the following section, we have, at times, had to rely on laboratory data which might not be applicable to full-size plant operations.

Below are listed those sources from which data has been obtained:

POMONA, CALIFORNIA

The Pomona installation is a Densator pilot plant, operated by the Los Angeles County Sanitary District. Data was obtained during the early part of 1968. However, its primary purpose was for conditioning water for input to ion exchange columns, P removal being a secondary consideration.

Operating data was obtained for the period March-May 1968. These consisted of input and output pH, alkalinity, Ca, total and ortho-P, and lime doses (all daily averages). The effluent values were given both unfiltered and filtered (sand) and the pH range covered was from 9.1 to 11.4.

This information is presented in Table 1.

TABLE 1

POMONA DATA*

pH			ALKALINITY mg/l $CaCO_3$			HARDNESS mg/l $CaCO_3$			CALCIUM mg/l $CaCO_3$			TOTAL PHOSPHORUS mg/l P			ORTHO-PHOSPHORUS mg/l P		
S	D	F	S	D	F	S	D	F	S	D	F	S	D	F	S	D	F
7.5	10.5	10.4	252	192	192	200	168	130	-	-	-	13.7	0.85	0.17	11.4	0.05	0.05
7.4	10.7	10.6	248	208	168	206	126	132	-	-	-	9.3	-	-	-	-	-
7.4	10.3	10.3	260	212	212	208	120	128	-	-	-	13.4	1.01	0.10	3.8	0.07	0.03
7.3	10.2	10.4	264	196	204	210	116	132	-	-	-	9.8	1.89	0.13	8.5	0.15	0.06
7.4	10.7	10.6	264	216	228	192	110	140	-	-	-	12.9	1.92	0.20	9.8	0.07	0.08
7.5	11.4	11.4	280	256	268	204	148	176	-	-	-	-	-	-	-	-	-
7.5	10.2	10.3	264	208	216	200	106	124	128	96	96	10.8	2.8	0.23	8.5	0.10	0.15
7.5	10.6	10.3	280	220	208	198	106	-	104	96	-	12.1	1.96	0.24	8.8	0.16	0.16
7.5	10.7	10.1	268	220	220	208	140	130	124	118	100	10.5	3.9	0.35	7.8	-	0.13
7.6	11.0	10.9	272	236	216	196	144	130	98	108	100	-	1.3	0.33	8.1	0.12	0.03
7.4	10.7	10.6	260	228	208	204	138	134	100	122	110	-	-	-	-	-	-
7.3	10.5	10.5	252	224	208	204	138	132	165	120	108	-	-	-	-	-	-
7.5	10.5	10.4	269	221	218	196	141	130	131	102	100	10.8	-	0.16	8.5	0.10	0.07
7.3	10.2	10.1	264	228	220	214	148	136	135	104	102	12.1	2.1	0.20	9.5	0.13	0.13
7.4	10.2	10.2	252	232	228	206	136	134	100	104	100	14.7	0.91	0.36	9.8	-	0.13
7.5	10.2	10.1	252	224	224	198	150	146	145	102	100	9.5	-	0.15	8.2	0.10	0.10
7.4	10.4	10.3	260	216	212	210	146	138	165	110	106	-	-	-	9.5	0.11	0.11

* S = Secondary Effluent
D = Densator Effluent
F = Filter Effluent

TABLE 1

POMONA DATA (CONTINUED)*

pH			ALKALINITY mg/l $CaCO_3$			HARDNESS mg/l $CaCO_3$			CALCIUM mg/l $CaCO_3$			TOTAL PHOSPHORUS mg/l P			ORTHO-PHOSPHORUS mg/l P		
S	D	F	S	D	F	S	D	F	S	D	F	S	D	F	S	D	F
7.6	10.0	9.9	-	-	-	205	155	150	-	-	-	10.2	-	0.29	8.3	0.20	0.20
7.3	9.8	9.8	274	272	268	198	173	171	129	124	121	12.4	3.1	0.31	10.4	0.42	0.31
7.4	9.6	9.7	268	260	244	204	172	180	160	122	136	10.0	2.8	0.49	8.9	0.36	0.32
7.5	9.7	9.6	286	224	240	216	158	156	150	132	122	10.0	-	0.52	8.2	-	0.39
7.5	9.3	9.4	260	244	236	206	148	162	175	120	120	10.4	2.1	0.72	7.5	0.65	0.32
7.4	9.5	9.6	274	256	244	206	168	180	96	102	104	13.4	4.0	0.72	9.5	0.65	0.52
7.4	9.4	9.4	280	240	248	210	160	180	145	104	140	10.0	-	0.59	8.2	0.72	0.52
7.5	9.5	9.4	284	277	267	203	182	181	148	125	126	9.1	2.9	0.56	7.5	0.59	0.49
7.4	9.7	9.6	264	240	244	208	156	168	-	-	-	10.8	3.3	0.47	9.1	0.57	0.36
7.4	9.5	9.4	274	212	192	190	185	170	124	120	156	13.1	6.5	0.65	10.4	0.62	0.46
7.5	9.3	9.3	268	280	272	208	192	212	-	-	-	21.9	3.3	0.62	8.2	0.52	0.49
7.5	9.1	9.2	275	255	202	210	224	206	144	135	116	10.8	8.2	3.6	8.8	0.73	0.60
7.4	9.1	9.1	272	304	296	204	196	218	-	-	-	10.0	5.6	0.9	8.0	0.90	0.62
7.6	9.4	9.5	276	288	288	212	180	208	92	124	152	13.7	12.4	0.78	10.1	0.91	0.65
7.4	9.3	9.3	264	264	256	204	180	184	98	104	106	12.1	6.5	0.78	8.2	0.69	0.52
7.4	9.2	9.2	256	300	288	208	208	216	-	-	-	9.8	10.6	0.59	7.7	0.81	0.55

* S = Secondary Effluent
D = Densator Effluent
F = Filter Effluent

BLUE PLAINS, WASHINGTON, D. C.

The Blue Plains installation is a joint FWPCA-D.C. tertiary treatment pilot plant. It has two Densators, operating at 54 gpm, with provisions for recarbonation between the two units. The bulk of the data given us (by Mr. D. F. Bishop, Plant Chief) was for P removal around the first unit only. Indications were that little, if any, further P removal was accomplished with two-stage operation. The plant is described in the report "Status and Outlook for Phosphorus Removal from Waste-Water" by Mr. Bishop(13).

Mr. Bishop supplied us with operating data and analyses for various treatment modes, as shown in Table 2. In addition, we were given access to the results of laboratory jar tests performed by Mr. Bishop on the secondary effluent. These results will be presented and commented upon in a later section of this report.

LAS VEGAS, NEVADA

The Nevada Power Company has been using lime clarification of secondary effluent for several years to produce cooling tower makeup water. Mr. James Zornes, Production Manager, was contacted and supplied us with typical influent and effluent analyses and operating parameters for the Sunrise Station. This plant utilizes an Eimco Reactor-Clarifier (a solids-contact-type precipitator) housed in a 60 ft. diameter basin. It is designed for an average flow of 2.5 mgd, and utilizes an average lime dose of 1 ton/million gallons. A flocculant aid, Nalco 603, is used at a dose of 3 mg/l. The average effluent pH is 10.0, and a residual total P level of 1.95 mg/l (as PO_4) is achieved in the clarifier. The clarifier effluent is not filtered, but is piped to a 6 million gallon reservoir for storage and settling. P analysis on the reservoir effluent was 1.25 mg/l (as PO_4).

Capital and operating cost figures were given both for this plant and another, the Clark Station. However, the capital figures did not seem consistent with those developed by us (see p. 25) and the chemical treatment costs were not consistent with the doses specified. Therefore, these figures were not used in our cost correlations.

LEBANON, OHIO

The Lebanon, Ohio plant is operated by the FWPCA for study of various advanced treatment techniques. One of the installations is a 0.1 mgd upflow lime clarifier, the main purpose of which is to investigate removal of suspended material rather than P removal. The effluent from the reactor is passed through dual media filters for final clarification.

While for the most part this unit is normally run at rather low pH levels (9-9.5), a series of experiments has recently been performed in which the pH was varied from 9.0 to 11.0. Mr. Edward L. Berg, the engineer in

TABLE 2

BLUE PLAINS PILOT PLANT

Mode	Raw	1st Stage 1A	2nd Stage 1A	Raw 2A	Clar 2A	Raw 3A	Clar 3A	Raw 4A	Clar 4A	Raw 5A	Clar 5A	Raw 6A	Clar 6A
Total Phosphorus (mg/l as PO_4)	22	2.4	2.4	20	1.5	21	0.94	19	1.1	21	2.2	21	1.2
T.O.C. (mg/l as C)	39.0	20.8	18.2	34	15.4	19.4	9.6	32	15.8	36	16.0	37	14.2
Suspended Solids (mg/l)	46	26	21	58	16	38	2.4	76	21	42	18	60	14
Mg^{++}(mg/l as Mg)	6.3	1.4	1.4	6.3	1.5	8.7	0.0	8.6	0	9.0	1.6	8.1	0.0
Ca^{++} (mg/l as Ca)	28.3	90.6	58.5	36	46	36	84	43	38	40	41	43	45
Turbidity J.T.U.	-	4.5	23	-	2.7	-	2.3	-	0.75	-	8.2	-	5.7
Alkalinity (mg/l as $CaCO_3$)	118	-	138	108	220	132	366	120	300	138	182	134	296
Temperature		22°C		24°C		24°C		28°C		27°C		26°C	
pH	-	11.4	10.0	11.2-11.5		11.2-11.5		11.5		11.0		11.5	
Flow (gpm)		34		54		54		54		54		54	
Lime Dose (mg/l as CaO)		200-300		200-300		200-300		200-300		150		200-300	
Soda Ash Dose (mg/l as Na_2CO_3)		None		175		175		175		175		175	
Recycle		None		None		None		10%		10%		10%	
Others		Two Stage		Na_2CO_3 to sec. zone		Na_2CO_3 to primary zone							

TABLE 2

BLUE PLAINS PILOT PLANT (CONTINUED)

Mode	1B Raw	1B Clar	2B Raw	2B Clar	3B Raw	3B Clar	4B Raw	4B Clar	5B Raw	5B Clar	6B Raw	6B Clar
Total Phosphorus (mg/l as PO_4)	18	1.5	23	4.5	24	2.4	28	4.9	26	5.5	28	9.2
T.O.C. (mg/l as C)	28	16.0	40	23	28	15.6	43	24	44	20	31	24
Suspended Solids (mg/l)	42	49	60	53	50	54	114	60	48	32	118	97
Mg^{++}(mg/l as Mg)	8.0	0.0	9.0	4.6	9.5	0	0	2.9	17	2.4	8.8	2.5
Ca^{++}(mg/l as Ca)	45	79	45	47	42	56	47	46	74	126	52	16
Turbidity (J.T.U.)	-	3.8	-	30	-	10.7	-	19.6	-	13.9	-	25.4
Alkalinity (mg/l as $CaCO_3$)	126	356	130	184	152	174	140	238	170	364	130	354
Temperature	24°C		24.5°C		24°C		23°C		22°C		20°C	
pH	11.5		11.0		11.0		11.5		11.7		11.7	
Flow (gpm)	54		54		54		54		54		54	
Lime Dose (mg/l as CaO)	200-300		150		150		200-300		300-400		300-400	
Soda Ash Dose (mg/l as Na_2CO_3)	225		225		225		225		225		225	
Recycle	None		None		None		None		None		None	
Others	None		None		5 mg/l Fe^{+3}		None		None		5 mg/l Mg^{++}	

charge of this unit, supplied us with phosphorus removal data (total P) around the clarifier unit, both filtered and unfiltered. This data indicated, as did that from Pomona, a strong dependence of P removal on pH. The specific data points obtained will be shown in the section on correlations below.

SOUTH TAHOE, CALIFORNIA

The treatment plant at South Tahoe has been amply described in the literature[9]. Briefly, it consists of a complete treatment facility including primary, secondary, and tertiary processes. P removal is accomplished in part by lime addition in the secondary (biological) step, and in part by further tertiary precipitation. Steps following the P removal process are ammonia stripping, filtration, and final polishing (activated carbon and chlorination). The tertiary P removal is not done in a solids-contact type unit. After lime addition, the reaction mixture is separately flocculated and then held in a settling basin where solids separation occurs.

Mr. R. L. Culp, General Manager, was contacted to obtain further information with respect to P removal in the tertiary lime addition step. He reported that optimum P removals were usually accomplished with a dose of about 400 mg/l lime, to a pH of 11.0. A polymer coagulant aid was also added after the precipitation reaction but before the flocculation basin. Residual P levels of about 0.15 mg/l were obtained.

CORRELATIONS

PERFORMANCE

The approach used in attempting to describe the expected performance of a tertiary lime addition process for P removal has been to arbitrarily separate the chemical processes from the solids separation processes. As explained in preceding sections of this report, this is undoubtedly a gross oversimplification. However, in light of the limited information available, this seems to be the most reasonable way to proceed. One should, of course, be cognizant of the possible errors involved in the assumptions and extrapolations which are used.

The procedure is to first determine the amount of all types formed by the chemical reactions. No distinction is made as to particle size or settleability. The sludge formed due to hardness, i.e., $CaCO_3$, $Mg(OH)_2$, etc. is calculated on the basis of standard chemical equilibrium concepts. As explained above, there appears to be no reasonable theoretical approach to describing the calcium phosphate precipitation. Therefore, the amount of calcium phosphate solids formed is derived on an empirical basis. Having determined the total amounts of various solids in the reactor, these are all handled equivalently in terms of physical separation, i.e., the fraction which is settled vs. the fraction which escapes into the effluent.

Chemical Phosphorus Removal

In examining the data concerning residual phosphorus levels, we have concentrated primarily on filtered, rather than unfiltered, effluents, as this gives a more realistic estimate of the conversion of P from soluble to insoluble form, independent of the physical separation processes occurring in the clarifier. (The distinction between solid and insoluble P, however, is arbitrary; solid phosphates of size small enough to pass a 0.45 micron filter are classified as "soluble", in terms of laboratory analyses. Effluents from plant filters will undoubtedly contain even larger particles, depending on the filter pore size and efficiency.)

Orthophosphate

The most convenient parameter which appears to correlate with the available data on residual soluble orthophosphate is pH. Figure 3 shows the results of plotting filtered residual orthophosphate vs. pH, using data points obtained from the Pomona unit, and those supplied us by Mr. D. F. Bishop for jar tests run on the Blue Plains secondary effluent. While the Pomona points are plant-filtered, the jar-test points are laboratory-filtered, using 0.45 micron filters. The equation for a least-squares regression line for these data is:

$$\text{Log } P_{ortho} \text{ (mg/l as P)} = 6.12 - (0.694)\ \text{pH} \qquad (5)$$

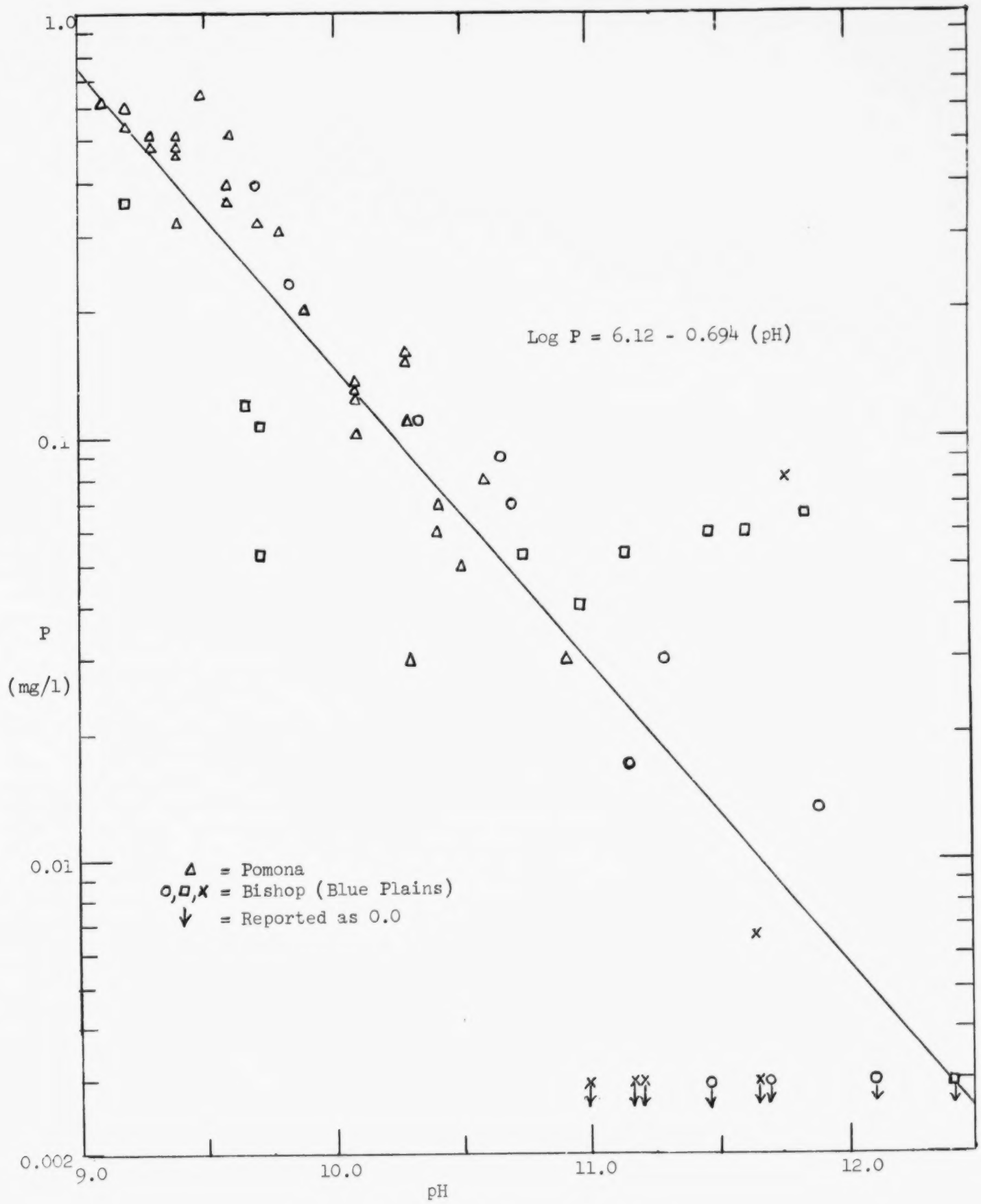


FIGURE 3. Filtered Ortho-P vs. pH

It is questionable, of course, whether the jar-test data points are valid in terms of predicting plant performance, especially in view of the very fine filters used. In other words, are the phosphate solids ($> 0.45\mu$) predicted by these data ultimately settleable even with the most efficient clarifier, or is some fraction permanently destined to appear in the effluent stream as colloidal material, regardless of the clarifier performance?

Total Phosphate

Residual total phosphate (ortho + condensed) values were also available from Pomona, and Blue Plains, and, in addition, some points were supplied by Mr. Edward Berg (Lebanon Lime Clarifier) and Mr. James Zornes of Nevada Power Company. Again, these were plant-filtered values, except for the NPC value, which was the effluent from a large settling basin, and for the Blue Plains jar test values, which were $0.45\ \mu$-filtered. The points from Lebanon are not raw data, but are taken from an already smoothed curve of P vs. pH.

These are plotted in Figure 4. Again, a relatively linear correlation with pH is obtained, the regression equation being:

$$\text{Log } P_{\text{total}} \text{ (mg/l as P)} = 3.51 - (0.392)\ \text{pH} \qquad (6)$$

As in the previous case, we have no values at the higher pH's except those of Bishop, which were $0.45\ \mu$-filtered. Again, therefore, it is not clear how much reliance may be put on these figures, in the pH range between 11 and 12, in terms of typical plant performance. This is borne out to some extent by examination of the Blue Plains Plant effluent analyses (Table 2) which show little, if any apparent pH dependence. On the other hand, it must be pointed out that the Blue Plains Plant is somewhat atypical in that the biological secondary process was quite unstable, leading to occasional high levels of organic solids and polyphosphates in the effluent. In addition, the Blue Plains water is extremely soft, which gave difficulty in maintaining a dense sludge. Soda ash, in varying amounts, was added to this water to increase the amount of sludge formed. For some of these cases, 5 mg/l Mg^{2+} and/or 5 mg/l Fe^{3+} were added, in an attempt to increase the efficiency of coagulation. Mr. Bishop informed us that Fe^{3+} was satisfactory for a time, but that the low density of the $Fe(OH)_3$ floc led to an increase in the volume of the sludge zone and ultimately to high solids carryover due to "scour" of the sludge by the water exiting the secondary reaction zone. Mr. Bishop also told us that recycle of sludge had no appreciable effect on P removal. As phosphate removal would appear to depend, to a large extent, on good solids separation, it is not clear why sludge recycle should be ineffective.

P vs. pH Relationship

Examination of the relations obtained for ortho-P vs. pH, and total P vs. pH indicates that ortho-P is removed more efficiently than condensed P.

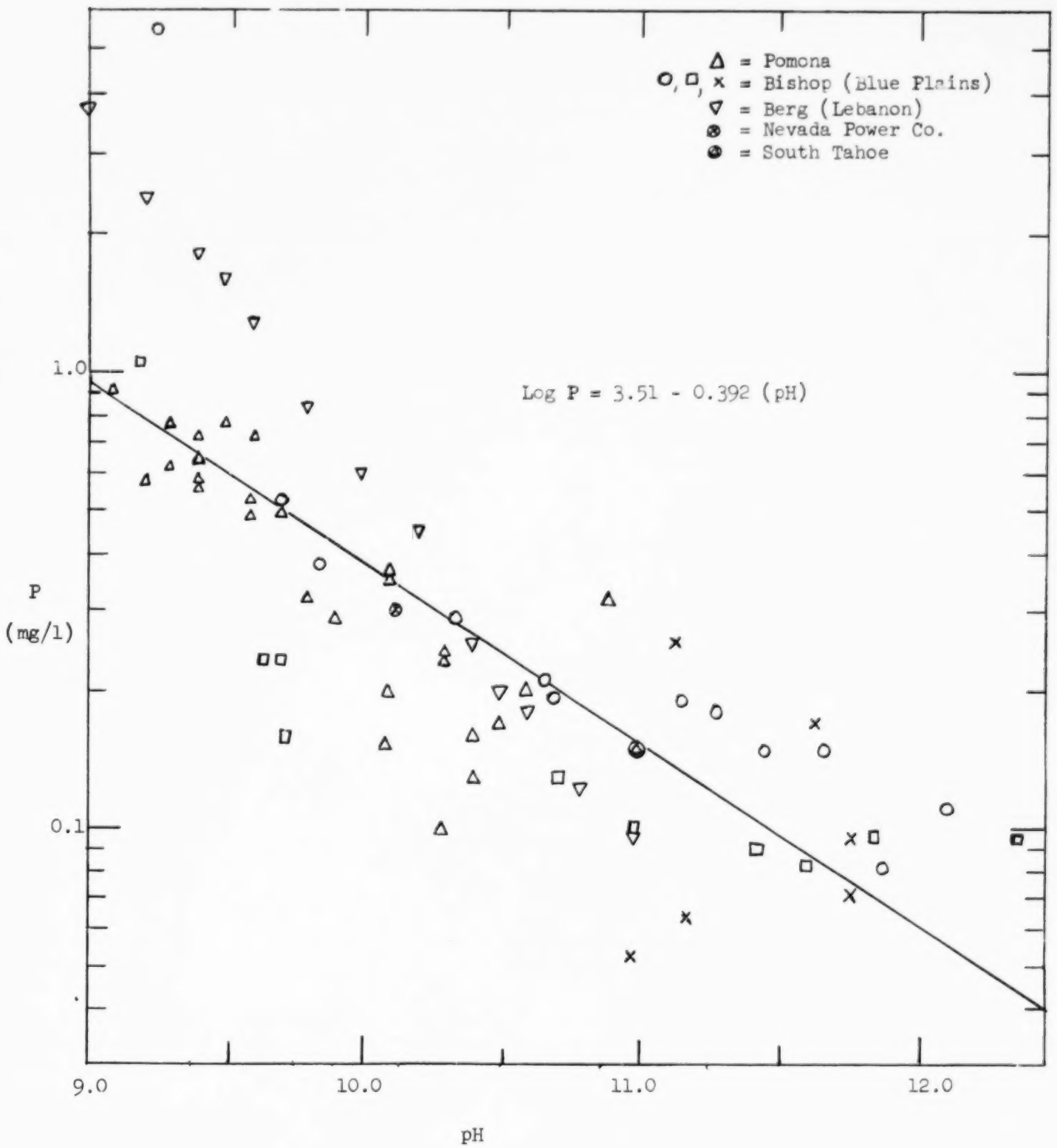


FIGURE 4. Filtered Total P vs. pH

This is probably true, although, as the primary mechanism of removal of the two species are different, i.e., precipitation and adsorption respectively, this will depend to a large extent on the particular operating conditions. Previous laboratory findings have indicated no significant difference between the removal of ortho- and condensed P by lime.

Use of both relations (5) and (6) simultaneously will result in an inconsistency; the difference between total and ortho-P (which is equal to condensed P) rises in the pH region between 9 and 10. Because the total P vs. pH relation is based on more actual operating data than the ortho-P relation, and in order to be somewhat more conservative than the jar test values in predicting ortho-P removal at the higher pH's, we have decided to use the total P correlation only, and to assume that the ratio of ortho/condensed P remains constant.

Calcium Carbonate Supersaturation

From the reported effluent analyses for Ca and alkalinity, it is possible to calculate the apparent Ca^{2+} and CO_3^{2-} concentrations (no correction being made for activity coefficient). Examination of almost all the data available to us, both laboratory and plant, show a (Ca^{2+}) (CO_3^{2-}) concentration product well in excess of the theoretical value, especially at high pH's.

Figure 5 is a plot of these calculated points, indicating a relatively linear rise up to pH~9.75, followed by a leveling off at a value of about 1.3×10^{-6} (theoretical value at 25° is about 1×10^{-8}). Such a large discrepancy cannot be accounted for, even allowing for activity coefficient corrections. This apparent supersaturation can be most easily described by the relation:

$$\text{Log } K = -6.7 + (pH - 9)(1.082) \qquad (pH \leq 9.75) \qquad (7)$$

$$\text{and } K = 1.3 \times 10^{-6} \qquad (pH > 9.75) \qquad (8)$$

where K is the apparent concentration product, (Ca^{2+}) (CO_3^{2-}).

Effect of Temperature

The effect of temperature on chemical equilibrium constants is described by the Van't Hoff Thermodynamic Equation (21).

$$\frac{d\,(\ln K)}{dT} = \frac{\Delta H^\circ}{RT^2}$$

where R = Gas constant, and

ΔH° = Energy term.

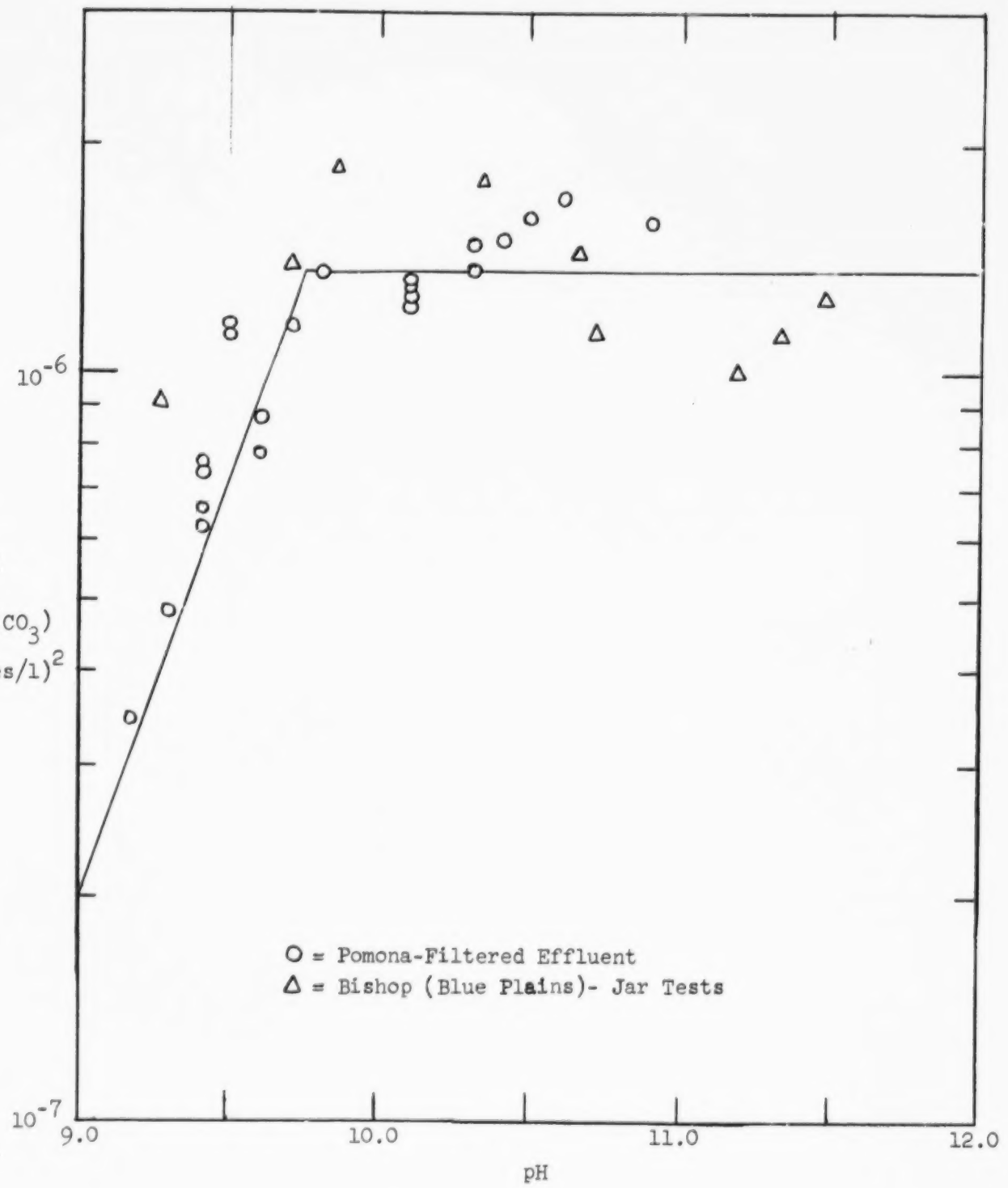


FIGURE 5. Apparent $(Ca)(CO_3)$ Solubility Product vs. pH

The energy term can be assumed constant in the small range of temperature, from 5°C to 30°C. The integration of the Van't Hoff relation yields

$$\log K = -\left(\frac{\Delta H^\circ}{4.576}\right)\frac{1}{T} + \left(\frac{\Delta H^\circ}{4.576\ T_o} + \log K_o\right)$$

or

$$\log K = \frac{a}{T} + b$$

The values of a and b were calculated from literature data[22] and softening plant data.

The relations between temperature and dissociation constants are given in Reference (23).

Coagulant Dose

In the absence of formation of enough $Mg(OH)_2$ to act as a coagulant and flocculating agent, it may be necessary, depending on the water composition, to add a coagulant. This might be one of a variety of materials including both inorganic and organic compounds.

Not enough information is currently available to predict, on any theoretical basis, the dose or type of coagulant which might be necessary; this information is usually adduced from jar tests on the specific water being treated. However, Infilco normally recommends the addition of coagulant if the $Mg(OH)_2$ formed is less than 50 mg/l. Using this as a working basis, and $FeSO_4$ as a typical coagulant, we will set up a relation whereby the $Mg(OH)_2$ "deficit" is made up by $Fe(OH)_2$ precipitate. On an equivalent molar basis, then, each mg/l difference between the $Mg(OH)_2$ formed and 50 mg/l will require 1.54 mg/l of $Fe(OH)_2$.

CAPITAL COSTS AND SIZING

The estimate of capital cost vs. treatment capacity was obtained on the following basis:

Approximate selling prices for Densators of various sizes were obtained from Infilco/Fuller. These prices were for the basic Densator Mechanisms, including: mixing chamber, agitators and sludge recycle pump, but did not include the costs of the external basins or other ancillary equipment. Also obtained were the recommended external basin dimensions and net rise areas.

Infilco recommends an overflow rate of 1.5 gal/min/ft^2 in application of this equipment to phosphorus removal by lime addition. Thus, one may calculate the treatment capacity of each unit, as in Table 3.

TABLE 3

DENSATOR PRICES VS. SIZE

Basin Diameter (ft)	Basin Depth (ft)	Net Rise Area (ft^2)	Approx. Selling Price ($)	Calculated Capacity (mgd)*
20	12-1/2	250	14,000	0.54
40	12-2/3	1068	25,000	2.3
60	14	2280	45,000	4.9
90	17-1/2	5120	70,000	11.0
120	18-1/2	9350	100,000	20.2

The approach used in estimating the costs of the construction and materials for the external basins was as follows: For concrete basins, the necessary wall thicknesses were calculated from the basin dimensions and water heights by using the standard engineering formula:

$$t = \frac{pr}{200} \qquad (9)$$

where t is the minimum wall thickness in inches for a concrete tank of radius r (inches) subject to a radial pressure p (psi). A minimum thickness of 8" was used for the smallest tank, and the values computed for the other tanks were rounded to the next highest inch. The volumes of the concrete shells were then calculated, together with a nominal 1 ft. thick tank bottom, and multiplied by an estimated cost of $81/cubic yard to obtain the costs for the outer basins. Added to these were the estimated costs for wooden pouring forms ($0.70/$ft^2$ contact area) and excavation and backfill for setting the basins 4 feet into the ground ($1.00/$yd^3$ and $0.50/$yd^3$, respectively).

A similar method was used for the steel basins. In this case, the formula:

$$t = \frac{pr}{15,000} + (1/16 \text{ to } 1/8) \qquad (10)$$

was used for calculating the wall thickness, with a minimum of 3/16" for the smaller basins.

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* Note that, if the 1.5 gal/min/ft^2 rise rate is not to be exceeded, these are <u>maximum</u> capacities.

The weight of the steel was then calculated (allowing 3% for overage) and an estimated cost of $0.28/lb (erected in place) was used to compute the total cost of the shell. Again, a 1 foot concrete floor was assumed for all cases, and the basins were assumed to be set 4 feet into the ground.

Table 4 gives the results of these calculations, with the figures conservatively rounded:

TABLE 4

ESTIMATED COSTS FOR DENSATOR INSTALLATIONS

CONCRETE BASIN

Capacity (mgd)	Shell	Bottom	Forms	Excav. & Fill	Basin Total	Total $\bar{w}$ Densator
0.54	$ 1,650	$ 1,100	$ 1,100	$ 100	$ 4,000	$ 18,000
2.3	4,400	4,100	2,500	300	11,300	36,300
4.9	8,000	9,100	3,800	600	21,500	66,500
11	26,500	21,000	7,000	1,200	56,000	126,000
20.2	33,500	37,000	10,000	2,000	102,500	202,500

STEEL BASIN

Capacity (mgd)	Shell	Bottom	Excav. & Fill	Basin Total	Total $\bar{w}$ Densator
0.54	$ 1,700	$ 950	$ 100	$ 2,750	$ 16,750
2.3	3,500	3,800	250	7,550	32,550
4.9	7,550	8,500	550	16,600	61,000
11	21,250	19,000	1,100	41,350	111,350
20.2	40,000	34,000	1,900	75,900	175.900

It will be noted that the costs of the steel shells are somewhat lower than for concrete; however, it appears that engineering practice favors concrete over steel for basins larger than about 40 ft. in diameter (possibly

because of problems in maintaining dimensional stability). We therefore have used the costs for steel basins up to this size, and for concrete basins for the larger sizes. These costs are plotted in Figure 6, together with the second order polynomial function which was calculated for the best least-squares fit:

$$\text{Log}_e \text{ Cost } (\$) = 1.0/(0.099485 - 0.005877 (\text{Log}_e Q)) \qquad (11)$$

where Q is the capacity of the unit in mgd.

The balance of the capital costs will also include ancillary equipment such as lime and coagulant feeding mechanisms. Examination of previous cost estimates for this type of system, as supplied by Infilco[14], indicate that the chemical feeding and control equipment will in general constitute no more than 3-5% of the capital cost for the Densator installation. Therefore, in the computer program, the capital costs derived above are multiplied by 1.05. Note that they do not include the cost of buildings, land, etc.

The capital costs are presented, both here and in the computer program, without conversion into amortization costs; it is expected that the calculation will be performed by the FWPCA Executive Program, and appropriately added to the total treatment cost.

It is of interest to compare the costs obtained above with those presented in previous estimates. The most recent estimate by Smith[15] appears in a report issued in July 1968. The corresponding capital costs (in those regions where the estimates overlap) are:

Capacity (mgd)	Smith	This Report
0.5	$ 50,000	$ 16,800
5	210,000	68,250
10	390,000	115,500
20	725,000	225,750
30	1,050,000	346,000

At first glance, there appears to be a discrepancy of about a factor of three between the two sets of figures. However, if one examines the references on which the first set of figures are based[14], one finds that they are computed for average flows for the Blue Plains sewage treatment plant, where the expected peak to average flow ratio is about 3. As stated above, the figures derived for this report are for maximum capacity. With this factor taken into consideration, the agreement is quite good.

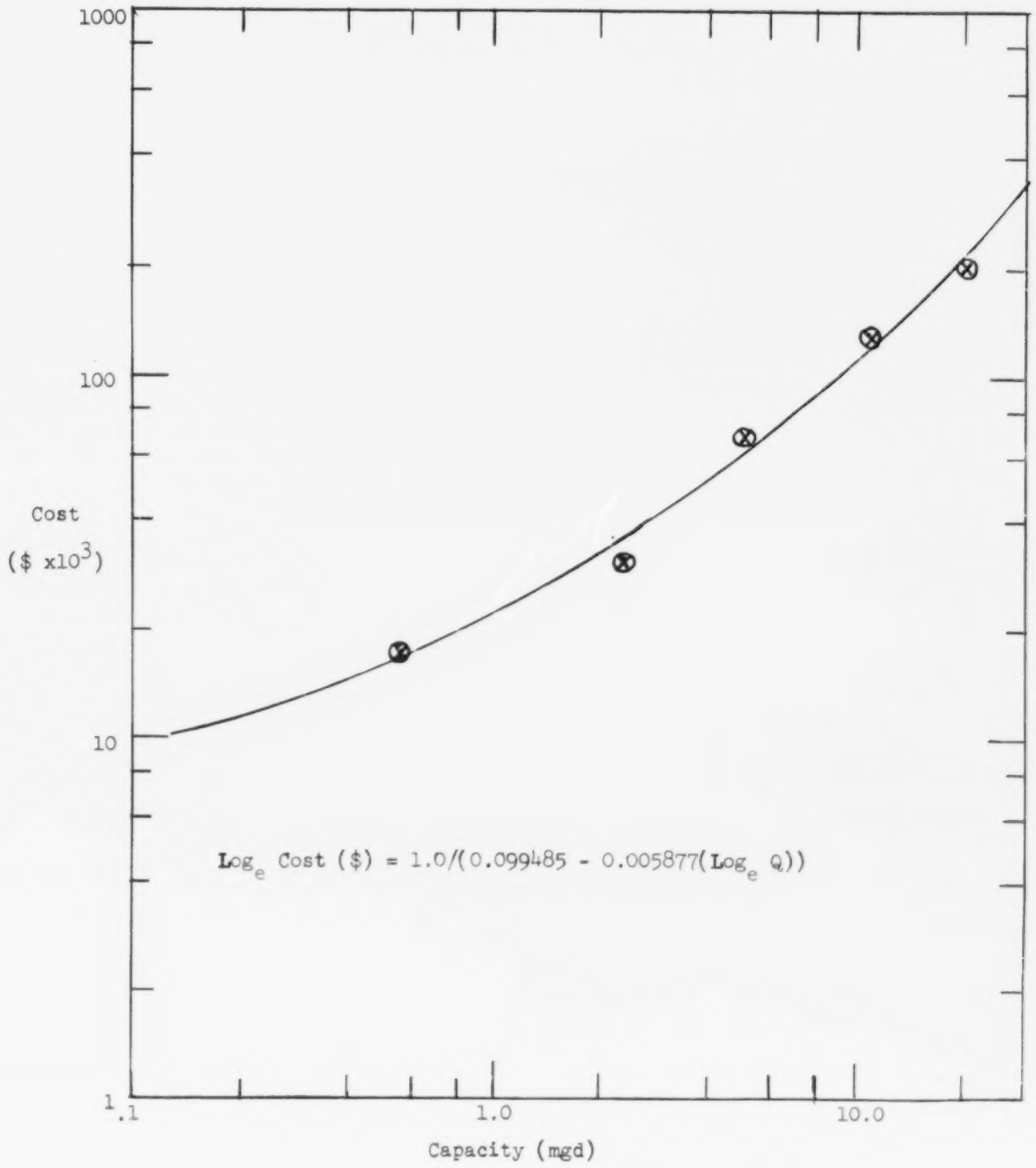

FIGURE 6. Capital Cost vs. Capacity for Densators, not Including Chemical Feed and Control Mechanisms.

Examination of the cost vs. capacity curve shows that a capacity of 30 mgd is, economically, about the maximum size for a single unit. For capacities greater than this, it is probably more practical to have several smaller units rather than one large unit.

OPERATING COSTS

In addition to the cost of chemicals (which will be computed from the chemical model), operating costs will include labor and power costs.

The cost of power has been estimated, again from figures supplied us by Infilco, for the total connective horsepower associated with the mixing, scraping, and recirculating mechanisms for the Densators of various sizes as given above. Figure 7 presents these figures, together with the approximation for Power vs. Capacity derived from these points:

$$HP = \frac{14}{11} \times Q \qquad (Q \leq 11 \text{ mgd}) \qquad (12)$$

$$HP = 14 + 0.06\,(Q - 11) \qquad (Q > 11 \text{ mgd}) \qquad (13)$$

Appropriate conversion factors may then be used to convert these into costs per 1000 gallons treated:

$$PWRCO \text{ (power cost in } \not{c} \text{ per 1000 gallons)} = HP \times CKWH \times 24 \times 0.746/(10^3 \times Q) \qquad (14)$$

where CKWH is the cost of electricity in cents/kwh.

The cost of operating labor will depend in large measure on the location of the installation with relation to other treatment processes. If it is in an integrated treatment plant, then it is possible that operators will be able to divide their time between Densator operation and other processes. However, especially with a pilot-plant type installation, which may be in a separate area, it may be necessary to keep operators on the site continually even when their services are not wholly occupied with the Densator.

It would seem somewhat more reasonable to relate the operating labor to the number of units to be attended, rather than to the plant capacity. (These, of course, are related through the sizing rule given above.) For example, it would probably take little, if any, more operating labor for a 10 mgd unit than for a 1 mgd unit. Previous estimates, supplied by Infilco[14][16], indicate that at least 0.5 man per shift would be needed for one unit, while for a multi-unit installation, the required labor appears to be about 1/10 man per shift per unit:

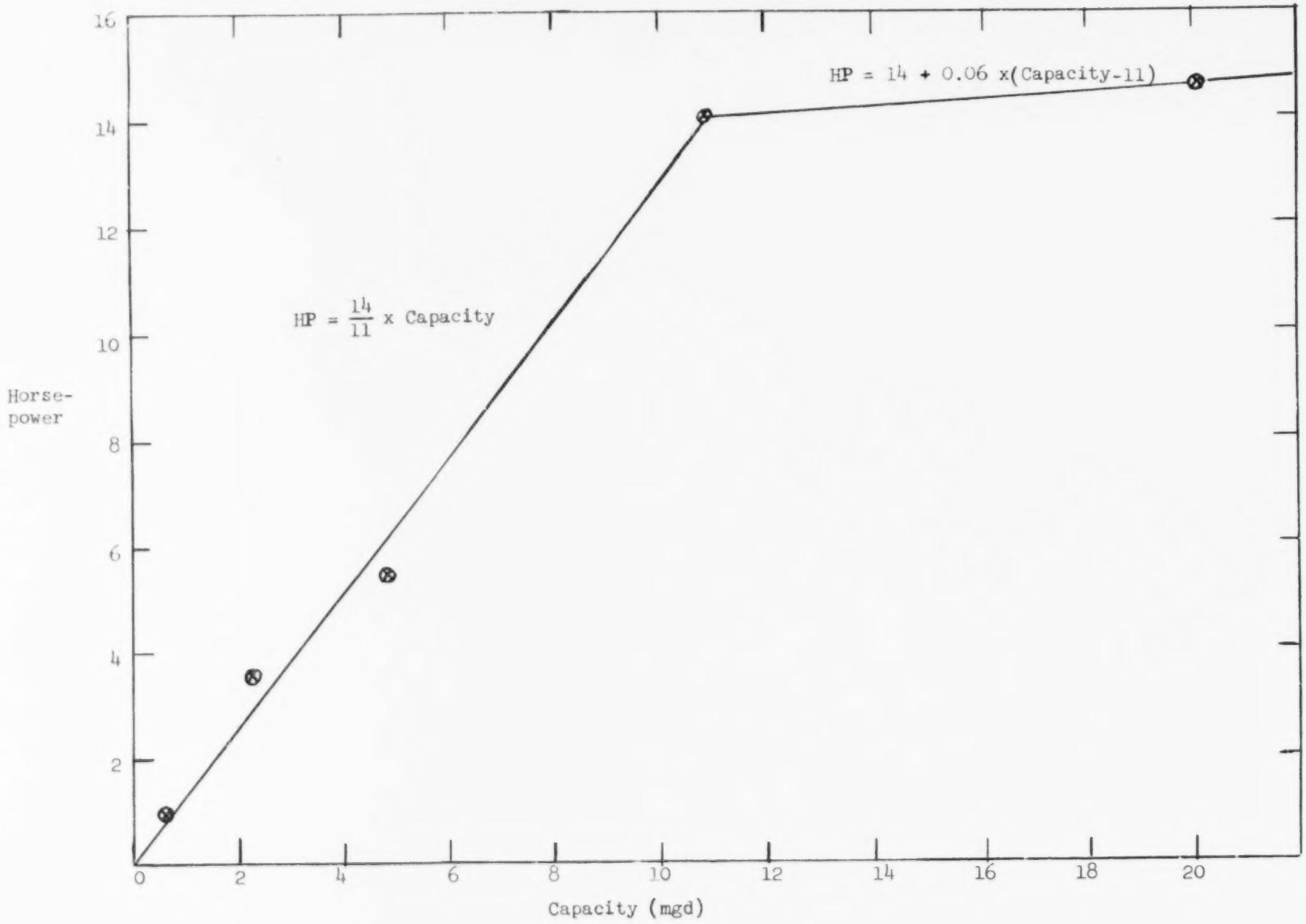

FIGURE 7. Horsepower vs. Capacity for Densators

TABLE 5

OPERATORS PER SHIFT FOR MULTI-UNIT INSTALLATIONS

Number of Units (N)	Operators
1	0.5
23	2
32	3
41	4

This relationship may be approximated (Figure 8) by the equation:

$$\text{Operators per Shift} = 0.5 + \frac{(N)^{1.365}}{46.35} \qquad (15)$$

Converting this into treatment cost:

$$\text{COLKG} = \left[\frac{\text{COLAB}}{2600 \times \text{QIN}}\right] \left[1.5 + \frac{(N)^{1.365}}{15.45}\right] \qquad (16)$$

where COLKG = labor cost (¢/1000 gal)

QIN = plant flow (mgd).

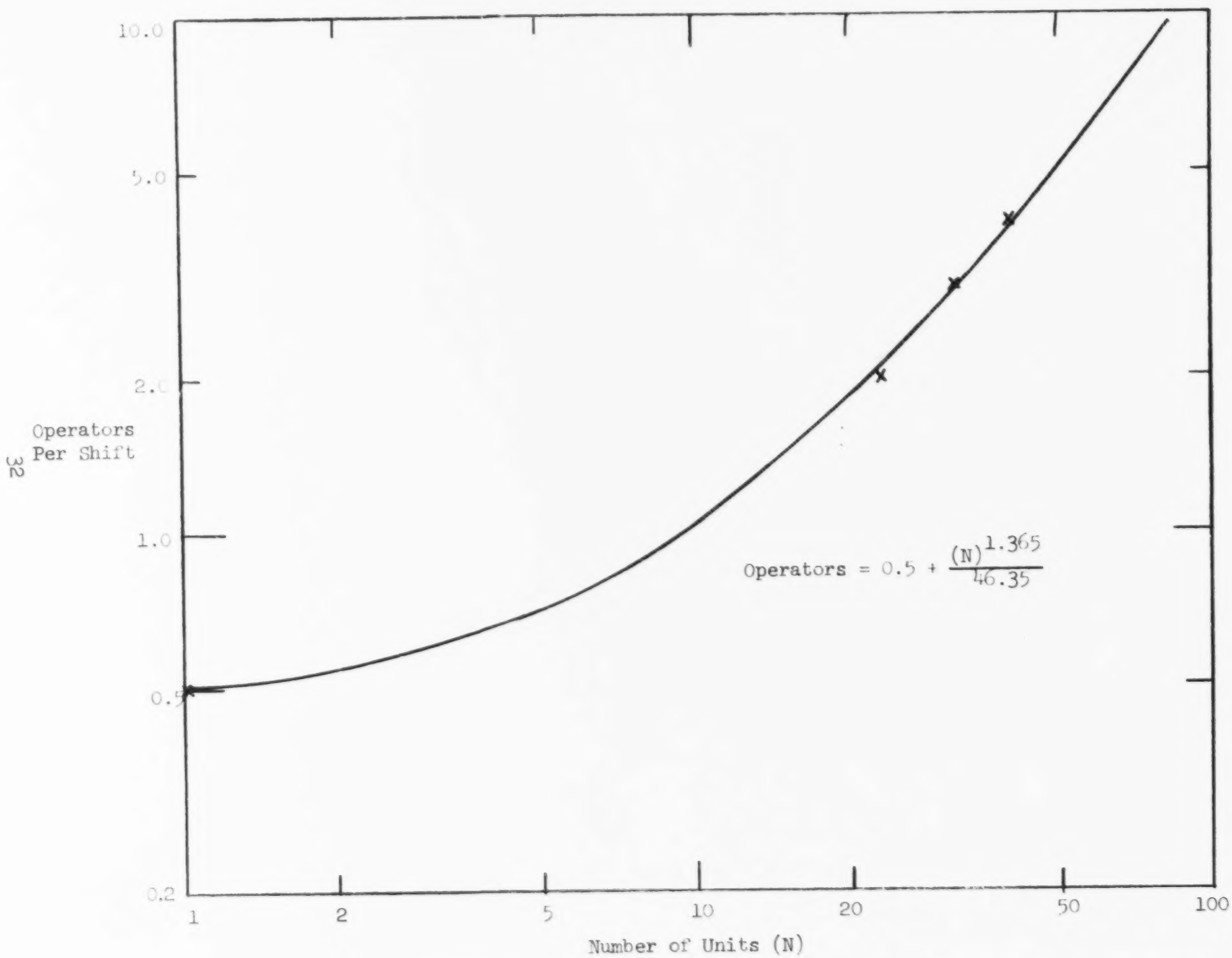

FIGURE 8. Operators Needed vs. Number of Units

METHODOLOGY USED IN COMPUTER PROGRAM

On the basis of the above equations, correlations and assumptions, the computer program (a listing for which is given in Appendix A) was derived. A brief description of this program is presented below.

INPUT

The input stream characteristics are read in on three cards, in F10.3 format. These include QIN, SOC, SON, SOP, SFM, SBOD, VSS, TSS, DOC, DNBC, DN, DP, DFM, ALK, DBOD, CA, MG, PH, AMO, and ORTO. (See Appendix for definitions).

It is possible that neither DP (dissolved phosphorus) nor DN (dissolved nitrogen) are further classified as to ortho-P or ammonia-N. In this case, the data fields for these (ORTO, AMO) are left blank.

The operating characteristics are then read in on two cards. These include TSS1, PHF, SLDEN, COLIM, FCA, FMG, TC, CKWH, COLAB, PKTAV, and COFES.

If either one or both of the ORTO or AMO fields is empty, ORTO is set equal to 0.9 x DP and/or AMO is set equal to 0.8 x DN. These are reasonable assumptions, based on Neale's[17] survey of secondary waste effluent compositions.

CHEMICAL EQUILIBRIA

The ionization and solubility product constants for H_2O, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, H_2CO_3, HCO_3^-, NH_4^+, $Mg(OH)_2$, $CaCO_3$, and $Fe(OH)_2$ are then calculated at the operating temperature. The input concentrations of those species which will be manipulated in the program are changed from mg/l to moles/l.

In order to reasonably estimate the activity(γ) coefficients of the various ions, it is necessary to know the ionic strength of the solution. The activity coefficient of an ion may be calculated from the Debye-Huckel approximation[18]:

$$\text{Log}\,\gamma_j = \frac{-0.508\, z_j^2 \sqrt{\mu}}{1 + 0.328\, r_j \sqrt{\mu}} \qquad (17)$$

where γ_j is the activity coefficient of ion j, μ the ionic strength of the solution, and r_j and z_j are, respectively, a constant associated with the ion, and its charge. (The average experimental values of r_j are given in Ref. 24.) As the ionic strength of a solution is defined as $\mu_j = i/2 \sum z_j^2 C_j$, where C_j is the concentration of each ion j, and z_j its charge, μ cannot be accurately calculated without a complete knowledge of the concentrations of all ions present. Lacking this information, we make an initial guess of the ionic

strength from the alkalinity (ALK) and dissolved fixed matter (DFM). DFM, as described in Standard Methods[19], is a measure of the soluble residue after ignition to 600°C. We make the following assumptions:

a) During this ignition, about half the HCO_3^- present will be lost as CO_2 and H_2O ($2HCO_3^- \rightarrow H_2O + CO_2 + CO_3^{2-}$), yielding 30 mg fixed matter per mole HCO_3^-.

b) Phosphates will be converted to pyrophosphates ($P_2O_7^{4-}$) yielding about 87 mg fixed matter per mmole of P.

c) Ammonium salts will decompose on ignition, leading to loss of both NH_4^+ ion and the anion with which it is associated (average MW ≈ 45).

d) About half the OH^- present will be lost by decomposition ($2OH^- \rightarrow H_2O + O^{2-}$), leading to 8 mg fixed matter per mmole OH^-.

e) The solution will contain, on the average[17] 43 mg/l SiO_3^{3-}, which will decompose to yield 34 mg/l SiO_2 residue.

f) The dissolved nitrogen which is not ammonia-nitrogen is nitrate.

g) All orthophosphate is present either as HPO_4^{2-} or $H_2PO_4^-$.

h) The average contribution of condensed phosphate to the alkalinity is 20 mg/l (as $CaCO_3$) per mmole P[3].

i) The ionic strength due to Na^+, K^+, SO_4^{2-}, and Cl^- can be approximated by $\mu \approx 1.8 \times 10^{-5} \times$ mg/l (see Ref. 25).

Using the above assumptions, it is possible to calculate the ionic strength due to those ions about which no input information is given (Na^+, K^+, SO_4^{2-}, Cl^-, etc.), and then to add the contributions from the known ionic species.

Having estimated μ, the activity coefficients for all pertinent ionic species are then calculated. These, coupled with the ionization constants and the input pH, allow calculation of the concentration ratios between the various forms of orthophosphate, carbonic acid and ammonia.

The program next tests whether or not the solubility product constants for $CaCO_3$ and $Mg(OH)_2$ are exceeded in the input stream. This is unlikely, but if such is the case, we assume that these precipitates are present in colloidal, unfilterable, form. Thus, they will have contributed (erroneously)

to the alkalinity, Ca, and Mg analyses on the input stream. We, therefore, solve for these quantities (COLCA and COLMG) and remove them from the "true" ionic concentrations. A calculation is then made of the potential acidity (POHI) of the input stream.

The final pH value (PHF) is then substituted for the initial pH, and the amount of phosphorus remaining and precipitated is computed, using the total-P vs. pH relationship described in a previous section. (A limit of 12.5 is put on the final pH, as this corresponds approximately to the maximum solubility of lime[20].) The calcium associated with the phosphate precipitate is "removed" from the total calcium in solution. A Ca/P ratio of 1.7, based on the hydroxyapatite formula, is assumed for the orthophosphate precipitate, while a Ca/P ratio of 0.5 is assumed for the condensed phosphate.

Control next reverts to a recalculation of the ionic strength, activity coefficients, and polyprotic equilibria using the new (final pH values). The program then bypasses the "colloid" and phosphate calculations, and proceeds to an estimate of the amount of $Mg(OH)_2$ which will be precipitated at the final pH.

If the amount of $Mg(OH)_2$ formed is less than 50 mg/l (8.6×10^{-4} moles/l), a coagulant dose of $FeSO_4$ is calculated which will result in the formation of enough $Fe(OH)_2$ to make up the difference. The potential acidity (POH) of the final solution is then estimated, and from the values of $Mg(OH)_2$, $Fe(OH)_2$ and POH, the hydroxyl demand and a corresponding test lime dose are calculated. The Ca and Mg brought in by this dose are added to the solution, and the amount of $CaCO_3$ precipitated is computed. An iteration process then begins, in which the program goes back to recalculate new activity coefficients, $Mg(OH)_2$ and $Fe(OH)_2$ precipitates, final potential acidity and lime doses. When two successive calculated lime doses are within 1/2% of each other, the iteration procedure is satisfied.

After leaving the iteration loop, the program calculates the final equilibrium Ca, Mg, and carbonate concentrations. To conform to the apparent supersaturation with respect to $CaCO_3$ observed at high pH's, some of the $CaCO_3$ is made "colloidal" (COLF) so as to yield a $(Ca^{2+})(CO_3^{2-})$ concentration product consistent with these observations. The output CA and ALK analyses are adjusted accordingly.

Later in the program, all chemical species are reconverted from moles/l to mg/l for readout.

The handling of both solid and dissolved output stream species is relatively straightforward, with the exception of DFM and SFM. Here, as for the input fixed matter, correction is made for the decomposition of some of the inorganic salts upon ignition:

$$Mg(OH)_2 \longrightarrow MgO + H_2O$$

$$Fe(OH)_2 + 1/2\ O_2 \longrightarrow Fe_2O_3 + H_2O$$

$$2OH^- \longrightarrow O^{2-} + H_2O$$

$$NH_4\,X \longrightarrow NH_3 + HX$$

etc.

SOLIDS

The total amount of solid sludge formed (SLUDG) is computed from the sum of the $CaCO_3$, $Mg(OH)_2$, $Fe(OH)_2$ and calcium phosphate precipitates. To these are added the input solids (TSS) to obtain the total solids (SOLID) present in the reaction zone effluent.

As all solids are assumed to behave equivalently, specification of TSS1, the suspended solids in the clarifier effluent, determines the ratio of settleable to unsettleable solids of all types. Thus, all solid species present are multiplied by TSS1/SOLID, which is the separation factor (SEPN) describing the performance of the unit for solids removal. The products obtained are put into output stream 1 (the clarified effluent).

In a similar fashion, specification of SLDEN, the solids content (mg/l) of output stream 2, allows the calculation of SLDEN/SOLID = CONCN, which is a concentration factor, describing the degree of sludge concentration obtained in the unit. All solid species are multiplied by this factor to obtain their concentrations in output stream 2 (the sludge waste).

FLOW RATES

The average flow rates in output streams 1 and 2 (Q_1 and Q_2) are calculated from simple mass balances. (It should be pointed out, of course, that these average rates are not continuous. In normal operation, the clarifier runs with no sludge waste for most of the time, the entire input flow exiting through output stream 1, with intermittent periods of sludge waste, which maintains the sludge inventory at a relatively constant level.)

Setting up a mass balance for solids, the mass of solids entering the unit per day, plus the mass of sludge formed in the reaction per day, must equal the total amount leaving per day.

$$\text{i.e.}\quad (QIN)(SOLID) = (Q_1)(TSS1) + (Q_2)(SLDEN) \tag{18}$$

$$Q_2 = \frac{QIN\,(SOLID) - Q_1\,(TSS1)}{SLDEN} \tag{19}$$

Making a volume balance for water, the volume of water entering must equal the volume leaving:

$$QIN = Q_1 + f(Q_2) \tag{20}$$

where f = volume fraction of water in Q_2.

We have assumed here that for both QIN and Q_1, the solids contents are so small that essentially all the volume is water. (We have also neglected the water associated with the lime feed stream.) The sludge waste stream, however, is usually quite high in solids and appropriate correction must be made: Letting RSGCC equal the specific gravity of the solid sludge (gm/cm^3), then the volume fraction of solids in the sludge waste stream is

$$\frac{SLDEN \times 10^{-6}}{RSGCC}$$

Therefore, the fractional volume of water in the sludge stream is

$$1 - SLDEN \times 10^{-6}/RSGCC, \text{ or } 1 - \frac{SLDEN}{RSMGL}$$

where RSMGL is the solid density in mg/l ($RSGCC \times 10^{-6}$). Setting the input and output water volumes equal:

$$QIN = Q_1 + Q_2 \left(1 - \frac{SLDEN}{RSMGL}\right) \tag{21}$$

$$Q_1 = QIN - Q_2 \left(\frac{RSMGL - SLDEN}{RSMGL}\right) \tag{22}$$

Substituting (22) in (19), and solving for Q_2:

$$Q_2 = QIN\ (SOLID - TSS1)(RSMGL)/(RSMGL)(SLDEN - TSS1) + (TSS1)(SLDEN) \tag{23}$$

Q_1 may then be calculated from equation (21):

$$Q_1 = QIN - Q_2\ (1 - SLDEN/RSMGL) \tag{24}$$

The density of the solid sludge (RSGCC) is arbitrarily taken as 2.0. This sludge will usually consist primarily of $CaCO_3$, the density of which, depending on its crystalline form, is quoted from 2.9 to 1.8. The 1.8 figure is for the hexahydrate, which is probably the species which will predominate in formation from aqueous solution. The density of solid calcium phosphate is also not known precisely, although it is probably higher than that of $CaCO_3$. $Mg(OH)_2$ and $Fe(OH)_2$, being gelatinous, will have rather low densities.

From SLDEN and RSGCC, the specific gravity of the sludge stream (RO2) is readily calculated:

$$RO2 = 1.0 + (SLDEN)(RSGCC - 1.0)/RSMGL \tag{25}$$

Using the figures derived above, the program next computes the weight and volume of sludge wasted per thousand gallons of water treated.

COSTS AND SIZING

From the computed lime and coagulant doses and the chemical costs (COLIM and COFE), the amounts of chemicals used per day and their cost per thousand gallons are next calculated.

For sizing the plant, we need the ratio of peak to average flow. (It will be remembered that the capital costs for Densators were derived on the basis of maximum flow.) As noted above, we have taken 30 mgd as the maximum unit size.

To obtain the number of Densator units (NUMB), therefore, the program multiplies the average design flow (QIN) by the expected peak to average flow ratio (PKTAV) to obtain QMAX, and divides by 30 mgd, rounding off to the next highest integer if there is a remainder. The capacity of each unit (QEACH) is obtained by division of QMAX by NUMB. QEACH will of necessity fall within the range of the capacity-cost correlation (0.5 - 30 mgd) and the formula derived previously is then used to calculate the cost per unit (COSTE) and the total cost (TCOST).

The electrical power is determined by calculating the power for each unit (HPPER), and multiplying by the number of units which would be in operation for average flow (NUMAV), to obtain total power (THP). Multiplication by the cost of power, and appropriate constants, gives the power cost per thousand gallons.

The labor cost per thousand gallons is calculated from the number of units, the plant flow, and the operators salary, as described previously.

The program then prints the output data giving the stream parameters for Q_1 and Q_2, and the lime and coagulant doses, costs, sizing and sludge waste characteristics.

CONCLUSIONS AND RECOMMENDATIONS

GENERAL CONCLUSIONS

The addition of lime to secondary effluents is an effective procedure for reducing phosphorus concentrations. The residual dissolved phosphate level declines as a function of the pH to which the waste-water is treated, with about 0.15 mg/l P remaining at a pH of 11 (Figure 2). It is more correct to characterize the process by the value of the residual P level rather than by % P removal, as the former seems to be insensitive to the input P level.

An analysis of capital cost vs. size for a solids-contact precipitator indicates that 30 mgd is about the maximum economical size for this type of apparatus (Figure 6), beyond which it is desirable to use a multi-unit installation.

The bulk of the total treatment cost will be dictated by the chemical dose, which in turn is dependent on the chemical composition of the water being treated. Low alkalinity waters will require less lime to reach a given pH; however, the reduced amount of $CaCO_3$ sludge formed may result in reduced efficiency for removal of precipitated phosphate. Waters low in Mg may also require addition of coagulants, due to the absence of precipitated $Mg(OH)_2$.

In view of the minimal amount of data on which the model is based, there are several limitations which must be recognized in employing it. These are noted below.

LIMITATIONS OF THE MODEL

P vs. pH Relationship

The most prominent theoretical drawback to the correlation between residual P and pH used in this model is that it takes no account of the calcium concentration. In theory, one could hypothesize a Ca concentration of zero, and yet the model will still predict phosphorus removal (as calcium phosphate). In practice, however, since we are restricting the model to a lime addition process, this will never be the case; calcium is continuously added to the system by the lime, so that by the time the pH is in the range where the P removal process would be operative, there is always a supersaturation with respect to calcium phosphate.

This can be demonstrated by worst-case calculation to find the minimum Ca concentration which would result from lime addition. Figure 9 shows the calculated final Ca concentrations to be expected by addition of lime to water having an initial Ca concentration of zero, an initial pH of 7.0, and various initial bicarbonate alkalinities (from 50-400 mg/l as $CaCO_3$). The 400 mg/l case is well in excess of any expected alkalinity.

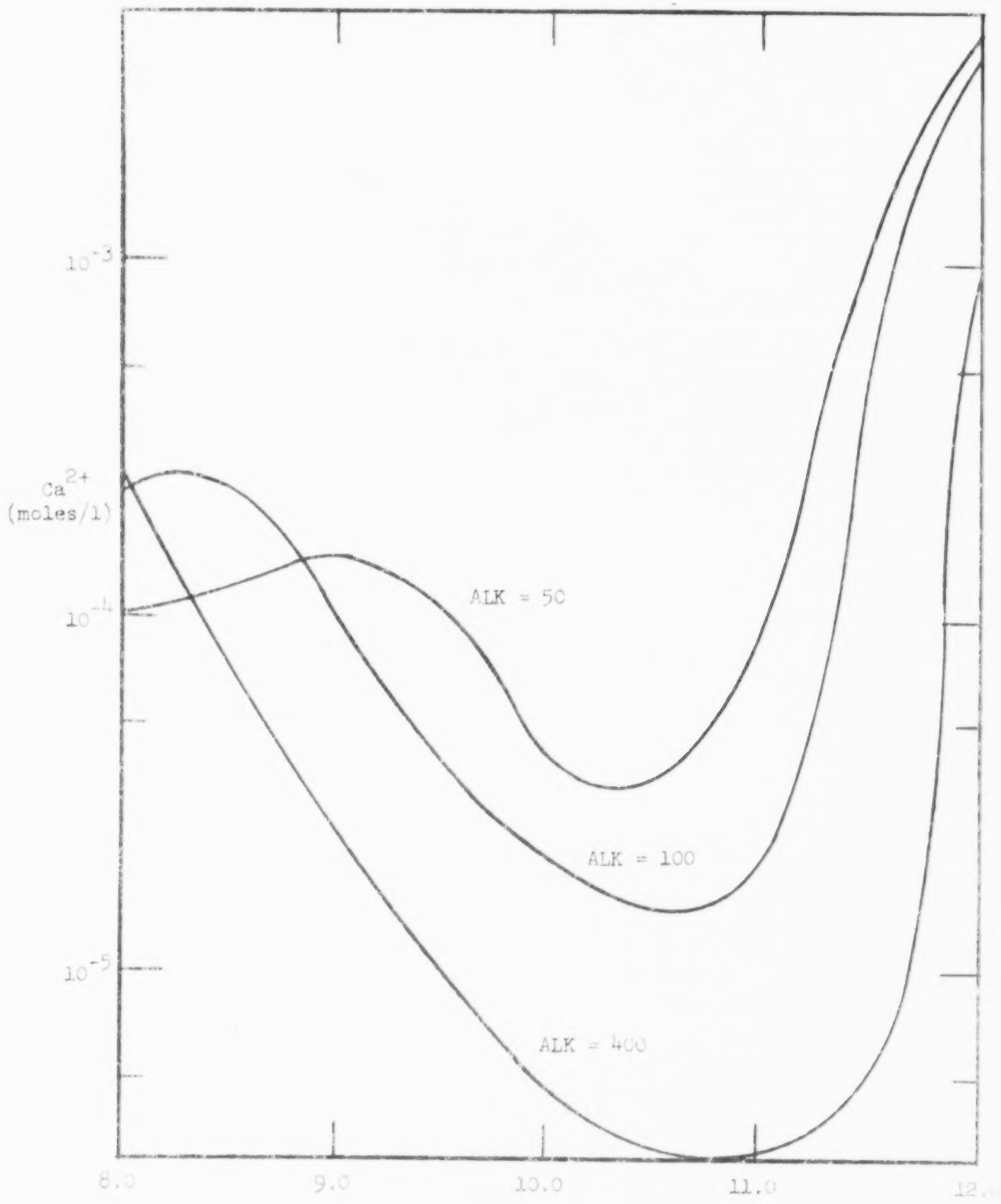

FIGURE 9. Minimum Ca Concentrations vs. pH.

For the low alkalinity waters, there is an initial increase in Ca content, followed by a decrease (as $CaCo_3$ is precipitated) and then followed by a sharp increase again when the carbonate is exhausted. It can be seen that the lowest Ca concentration is obtained with the highest alkalinity water. Even this low calcium level, however, is sufficient for supersaturation with respect to $Ca_{10}(OH)_2(PO_4)_6$, as it occurs at a Ph high enough so that: (a) there is a high OH concentration, and (b) a larger fraction of the orthophosphate present is in the form of $(PO_4)^{3-}$.

Figure 10 illustrates this point. Here, we have plotted the "maximum" equilibrium values of total orthophosphate consistent with the theoretical solubility product of $Ca(OH)_2$ $(PO_4)_6$, and the Ca values shown in Figure 9 for the worst case alkalinity of 400 mg/l.

Thus, while calcium ion concentration is not explicitly included in the P vs. pH relationship, we may be sure that there is always enough present to achieve supersaturation with respect to the precipitation of phosphate.

It should also be borne in mind that the P vs. pH correlation is based primarily on points taken in the pH region from 9.5-11.0. Extrapolation outside these limits should be made with care.

Solids Separation

Another assumption which has been made, and for which there is no confirmatory evidence, is that all types of solids (i.e., organics, phosphates, $CaCO_3$, etc.) are separated to the same degree by the clarifier. Because of the variations in size, density, etc. of these solids, this is unlikely; however, there is at present not enough information available to make any other assumption for the model.

In constructing the model, we have also been forced to skirt the issue of the physical separation process itself. Rather than predicting clarification performance, the model takes as an input TSSl, (the effluent suspended solids), thereby specifying performance. Again, this step has had to be taken due to the lack of any basic knowledge of the actions of a host of physical and chemical parameters on the processes of coagulation, flocculation and sedimentation. While there are many theoretical analyses and discussions of these processes available in the literature, one would be hard pressed to apply them to the case under consideration, lacking such information as the precipitate particle size distributions, densities of various precipitates, relation between "nominal" rise rates and actual liquid velocities in various parts of the sedimentation zone, etc.

Sizing

In line with the above comments, a word should be said about the use of the nominal rise rate of 1.5 gal/min/ft^2 in sizing the apparatus. This figure has been quoted as one which will yield efficient operation with minimal solids carry-over. However, there has been little, if any, work done on relating

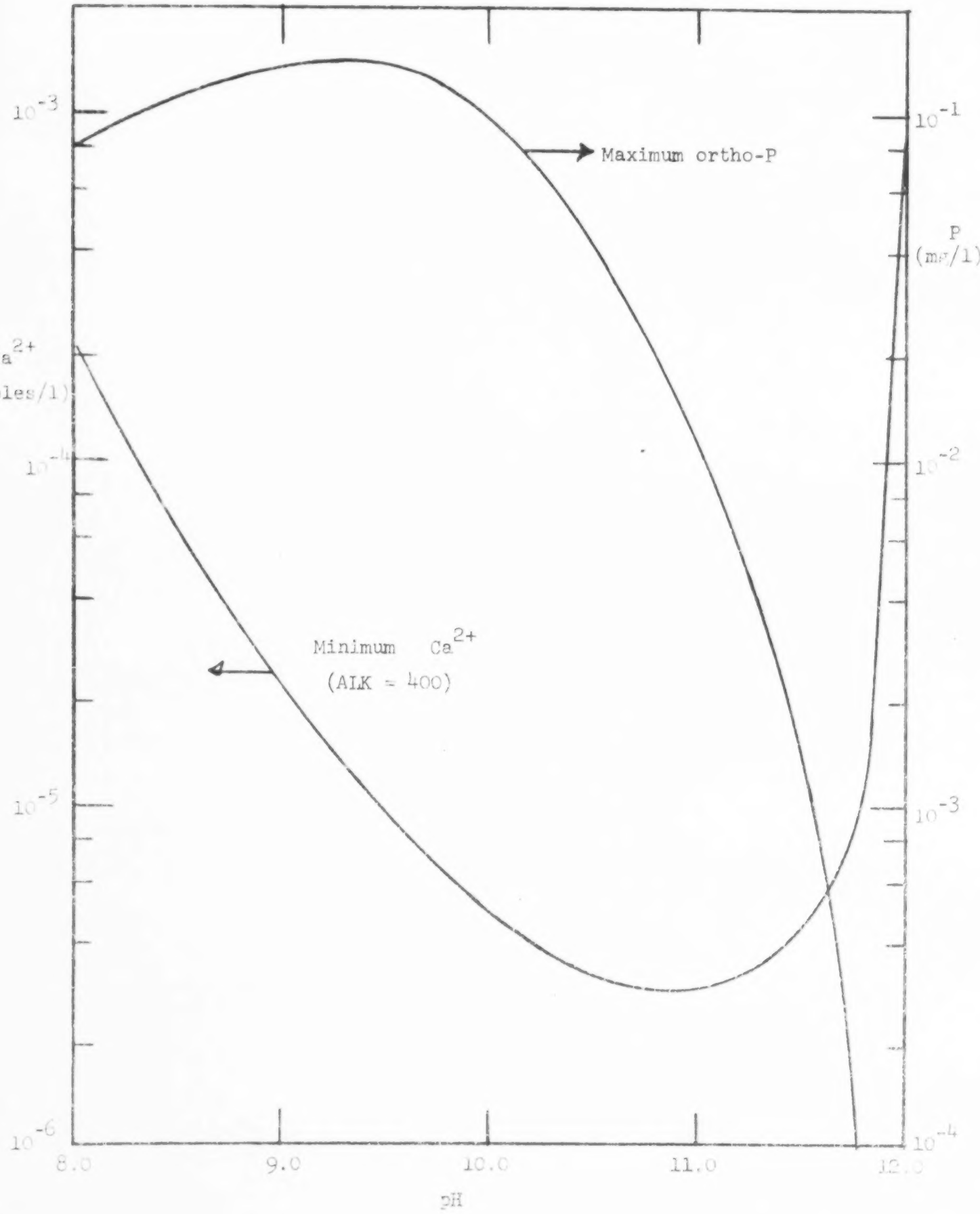

FIGURE 10. Theoretical P and Ca Concentrations vs. pH.

solids separation efficiency to residence times and rise velocities. If the lime addition process is followed by a filtration step, it might well be more economical to work at a higher throughput rate, sacrificing clarification efficiency, but decreasing the necessary apparatus size and capital cost. With no estimate of this relationship, however, it is impossible to predict whether or not such a trade-off would be feasible.

Coagulant

As noted above, $FeSO_4$ was taken as a typical coagulant, and its dose predicted on the basis of obtaining an arbitrary minimum concentration of combined $Mg(OH)_2$ and $Fe(OH)_2$ to aid in flocculation. Many other materials may also perform this function, and this report should not be interpreted as indicating that this is the coagulant of choice. With a K_{SP} for $Fe(OH)_2$ of $\sim 10^{-14}$, Fe^{2+} ion is efficient in forming a hydroxide floc at high pH's. However, at lower pH's ($\sim$ 9-9.5) only a portion of the added Fe^{2+} ion will form the hydroxide, leading to economically prohibitive calculated doses in order to obtain the minimum specified amount of $Fe(OH)_2$. This limitation should be recognized, and the possibility of using other materials considered. For example, on a cost per atom basis, ferric sulfate is much more expensive than the ferrous salt. However, the higher charge on the ferric ion makes it a more effective coagulant, while the much lower K_{SP} for the hydroxide ($\sim 10^{-33}$) means that, even at low pH's, essentially all the added Fe^{3+} will form $Fe(OH)_3$ floc.

SUGGESTIONS FOR FURTHER WORK

The above assumptions and limitations of the program, together with the reasons for them, are indicative of the areas where further work (both theoretical and applied) should be done.

It would be of interest, for example, to examine the compositions of both the effluent solids and the waste solids produced by an operating unit to see whether all types of solids are settled in the same ratio, and, if not, what the partition factor is for each type.

A study of the relationship between effluent solids and rise rate would also be of value in obtaining a more fundamental rationale for predicting effluent TSS.

In light of the marked variation in behavior with respect to P removal between soft waters such as at Blue Plains, and hard waters such as at Lebanon or Pomona, further study should be given to the effects of sludge density, $Mg(OH)_2$ and coagulants, on the P removal process. As Mr. Bishop at Blue Plains has obtained excellent removals in filtered jar test effluents, the problem appears to be associated with the solids separation process.

As more such tertiary treatment units come into use, more operational experience will be gained, and it is likely that more relevant experimental work will be done in this field. The increase in the amount of information available should then allow the development of a more generalized and complete model of the process than has been possible based on the present limited amount of data.

APPENDIX A

COMPUTER PROGRAM LISTING

SAMPLE PRINTOUT AND DEFINITION OF SYMBOLS

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```
// FOR
*IOCS(CARD,1132PRINTER,DISK)
*EXTENDED PRECISION
*ONE WORD INTEGERS
*LIST ALL
      REAL  MU,MURES,MG,MGOH2
      Y(R,Z,U)=10.0**((-0.508*Z**2*U)/(1.0+0.328*R*U))
   10 FORMAT(8F10.3)
   20 FORMAT (1H1,37X,26HP REMOVAL BY LIME ADDITION,///,1H0,45X,
     1  9HCASE NO. ,I2,/,1H0,45X,12HINPUT STREAM)
   21 FORMAT(1H0,9X,1HQ,10X,3HSOC,9X,4HSNBC,8X,3HSON,9X,3HSOP,9X,3HSFM,
     1  8X,4HSBOD,/,3X,7F12.4//9X,3HVSS,9X,3HTSS,9X,3HDOC,9X,4HDNBC,9X,
     2  2HDN,10X,2HDP,9X,3HDFM/,3X,7F12.4//9X,3HALK,9X,4HDBOD,9X,2HCA,
     3  10X,2HMG,10X,2HPH,9X,3HAMO,7X,7HORTHO-P,/,3X,7F12.4,//)
   22 FORMAT (1H0,44X,23HPROCESS CHARACTERISTICS,)
   23 FORMAT(1H0,7X,4HTSS1,9X,2HPH,8X,5HSLDEN,8X,5HCOLIM,8X,3HFCA,9X,
     1  3HFMG,8X,4HTEMP/3X,7F12.4//9X,4HCKWH,7X,5HCOLAB,7X,5HPKTAV,7X,
     2  5HCOFES/3X,4F12.4//)
   24 FORMAT (1H0,44X,15HOUTPUT STREAM 1)
   25 FORMAT (1H1,44X,15HOUTPUT STREAM 2)
   26 FORMAT (1H0,20X,' ORTHO-P NOT GIVEN.ASSUMED TO BE 0.9*DP.',/)
   27 FORMAT(1H0,20X,' AMMONIA NITROGEN NOT GIVEN.ASSUMED TO BE 0.8*DN')
   31 FORMAT(1H0,10X,' COSTS,SIZING,AND WASTE',//,' NO. OF UNITS = ',
     1  I4,//,' CAP COST PER UNIT = ',F10.3,' KDOLLARS',//,
     2  ' TOTAL CAP COST = ',F10.3,' KDOLLARS',//,' LIME DOSE = ',
     3  F10.3,' PPM',//,' LIME USED PER DAY = ',F10.3,' TONS',//,
     4  ' LIME COST = ',F10.3,' CENTS PER KGAL',//,' LABOR COST = ',
     5  F10.3,' CENTS PER KGAL',)
   32 FORMAT(1H0,' COAGULANT DOSE = ',F10.3,' PPM FESO4'//,
     1  ' FESO4 USED PER DAY = ',F10.3,' TONS'//' FESO4 COST = ',F10.3,
     2  ' CENTS PER KGAL'//' POWER COST = ',F10.3,' CENTS PER KGAL',//
     3  ' SLUDGE SPECIFIC GRAVITY = ',F10.3,' GMS PER CM3'//,
     4  ' SLUDGE WT PER KGAL TREATED = ',F10.3,' LBS'//
     5  ' SLUDGE VOLUME PER KGAL TREATED = ', F10.3,' GAL' )
  321 FORMAT (1H0,20X,' PH HAS BEEN LOWERED TO 12.5 DUE TO LIME SOLUBILI
     1LITY LIMIT',/)
      NCASE=1
  998 CONTINUE
      READ(2,10) QIN, SOC, SNBC, SON, SOP, SFM, SBOD, VSS, TSS, DOC,
     1  DNBC,DN,DP,DFM,ALK,DBOD,CA,MG,PH,AMO,ORTO
      IF (QIN) 999,999,991
  991 CONTINUE
      READ(2,10) TSS1,PHF,SLDEN,COLIM,FCA,FMG,TC,CKWH,COLAB,PKTAV,COFES
      WRITE (3,20) NCASE
      WRITE(3,21) QIN,SOC,SNBC,SON,SOP,SFM,SBOD,VSS,TSS,DOC,DNBC,DN,DP,
     1  DFM,ALK,DBOD,CA,MG,PH,AMO,ORTO
      WRITE (3,22)
      WRITE(3,23)TSS1,PHF,SLDEN,COLIM,FCA,FMG,TC,CKWH,COLAB,PKTAV,COFES
      IF(ORTO) 111,111,112
  111 ORTO=0.9*DP
      WRITE (3,26)
  112 POLY=DP-ORTO
      IF (AMO-.001) 113,113,114
  113 AMO=0.8*DN
      WRITE (3,27)
  114 CONTINUE
      TK=TC+273.0
      INT=0
      DOS=0.0
      EH2O=10.0**((-4471.33/TK)+6.0846-(0.017053*TK))
```

```
      EH3P=10.0**((-799.31/TK)+4.5535-(0.013486*TK))
      EH2P=10.0**((-1979.5/TK)+5.3541-(0.01984*TK))
      EH1P=4.8E-13
      EH2C=10.0**((-3404.71/TK)+14.8435-(0.032786*TK))
      EH1C=10.0**((-2902.39/TK)+6.498-(0.02379*TK))
      EMG=10.0**(1250.0/TK-15.145)
      ECACO=10.0**(483.0/TK-9.68)
      ENH4=10.0**((-2835.76/TK)+0.6322-(0.001225*TK))
      EFE=3.0E-14
      CA=CA/40080.0
      MG=MG/24310.0
      ALK=ALK/1.0E5
      ORTO=ORTO/30974.0
      POLY=POLY/30974.0
      TPHO=ORTO+POLY
      AMO=AMO/14007.0
      H=10.0**(-PH)
      UVW=2.0*EH1C+H
      XYZ=EH2P+H
      QRS=ENH4+H
      MURES=(1.8E-5)*DFM-1.08*ALK-ORTO*(1.57-0.54*EH2P/XYZ)-1.35*POLY
     1   +AMO*(0.616+(0.54*ENH4+0.81*H)/QRS)+0.396*EH2O/H-(6.12E-5)
     2   -0.616*DN/14007.0-0.721*CA-0.438*MG
      UNIV=2.0*ALK*H/UVW+EH2O/H*2.0*EH1C/UVW+ORTO*H/UVW*(UVW-EH2P)/XYZ
     1   +AMO*H/UVW*(UVW-ENH4)/QRS-0.4*POLY/UVW*H+H
      DIV=2.0*ALK/UVW*EH1C-EH2O/H*EH1C/UVW+ORTO*(EH1C+H)/UVW*EH2P/XYZ
     1   +POLY*(1.2*EH1C+H)/(2.0*UVW)-AMO*EH1C/UVW*ENH4/QRS+CA+MG
      TRIV=ORTO*EH1P/(EH1P*EH2P+EH1P*H+H**2)*EH2P
      GO TO 101
  100 UNIV=CAR*AL7/AL6+H+OH+AM4+ORTO*AL4/(AL2*AL3)
      DIV=MG+CA+CAR*AL7+ORTO*AL4/AL3+0.5*POLY+FE+FESO4
      TRIV=AL4*ORTO
  101 MU=MURES+0.5*UNIV+2.0*DIV+4.5*TRIV
      U=SQRT(MU)
      YH=Y(9.0,1.0,U)
      YOH=Y(3.5,1.0,U)
      YHCO3=Y(4.25,1.0,U)
      YCO3=Y(4.5,2.0,U)
      YCA=Y(6.0,2.0,U)
      YMG=Y(8.0,2.0,U)
      YH2P=Y(4.25,1.0,U)
      YPO4=Y(4.0,3.0,U)
      YHP=Y(4.0,2.0,U)
      YNH4=Y(2.5,1.0,U)
      YFE=Y(6.0,2.0,U)
      AH=10.0**(-PH)
      H=AH/YH
      OH=EH2O/(AH*YOH)
      AL1=EH3P/(AH*YH2P)
      AL2=EH2P*YH2P/(AH*YHP)
      AL3=EH1P*YHP/(AH*YPO4)
      AL4=AL1*AL2*AL3/(1.0+AL1+AL1*AL2+AL1*AL2*AL3)
      AL5=EH2C/(AH*YHCO3)
      AL6=EH1C*YHCO3/(YCO3*AH)
      AL7=AL5*AL6/(1.0+AL5+AL5*AL6)
      AL8=ENH4*YNH4/AH
      AL9=1.0/(1.0+AL8)
      AM4=AMO*AL9
      AM3=AMO-AM4
      INT=INT+1
```

```
      IF(INT-2) 700,100,800
  700 COLMG=MG-EMG/(YMG*(YOH*OH)**2)
      IF(COLMG) 710,710,720
  710 COLMG=0.0
  720 ALKCO=ALK-AL4*ORTO-0.5*AL4*ORTO/AL3-0.2*POLY-0.5*OH-COLMG-0.5*AM3
      XYZ=1.0+1.0/(2.0*AL6)
      UVW=ECACO/(YCA*YCO3)
      COLCA=0.5*(CA+ALKCO-SQRT((CA+ALKCO)**2-4.0*(CA*ALKCO-UVW*XYZ)))
      IF(COLCA) 730,730,740
  730 COLCA=0.0
  740 ALKCO=ALKCO-COLCA
      CAR=ALKCO/(XYZ*AL7)
      BCAR=CAR
      BMG=MG-COLMG
      MG=BMG
      AMG=BMG
      GO TO 300
  800 MGOH2=AMG-EMG/(YMG*(YOH*OH)**2)
      IF(MGOH2) 110,110,140
  110 MGOH2=0.0
  140 POH=ORTO*AL4*(3.0/(AL2*AL1)+2.0/AL2+1.0)/AL3+CAR*AL7*(1.0+2.0/AL5)
     1/AL6+H-OH+AM4
      FEOH2=(8.6E-4)-MGOH2
      IF (FEOH2) 141,141,142
  141 FEOH2=0.0
      FESO4=0.0
      GO TO 143
  142 FE=EFE/(YFE*(YOH*OH)**2)
      FESO4=FEOH2+FE
  143 DOSE=0.5*(POHI+2.0*MGOH2+2.0*FEOH2+0.33*SORTO-POH)
      IF(DOSE) 150,150,160
  150 DOSE=0.00001
  160 ABC=40.3*FCA+56.08*FMG
      CA=BCA+DOSE*40.3*FCA/ABC
      AMG=BMG+DOSE*56.08*FMG/ABC
      MG=AMG-MGOH2
      CAR=BCAR
      XYZ=4.0*ECACO/(AL7*YCA*YCO3)
      XYZ=(CA-CAR)**2+XYZ
      XYZ=SQRT(XYZ)
      CACO3=(CA+CAR-XYZ)/2.0
      IF(CACO3) 220,220,500
  220 CACO3=0.0
      GO TO 500
  300 POHI=ORTO*AL4*(3.0/(AL2+AL1)+2.0/AL2+1.0)/AL3+CAR*AL7*
     1    (1.0+2.0/AL5)/AL6+H-OH+AM4
      IF(PHF-12.5) 310,310,320
  310 IF(PHF-PH) 330,330,340
  330 PHF=PH
      GO TO 340
  320 PHF=12.5
      WRITE (3,321)
  340 PH=PHF
      XYZ=3.512-0.3924*PH
      STPHO=TPHO-10.0**XYZ/30974.0
      IF(STPHO) 430,430,440
  430 STPHO=0.0
  440 SORTO=STPHO*ORTO/TPHO
      BCA=CA-COLCA-1.7*SORTO-0.5*(STPHO-SORTO)
      CA=BCA
```

```
      FESO4=0.0
      FE=0.0
      TPHO=TPHO-STPHO
      ORTO=ORTO-SORTO
      POLY=TPHO-ORTO
      AH=10.0**(-PH)
      H=AH/YH
      OH=EH2O/(AH*YOH)
      GO TO 100
  500 CONTINUE
      CAR=BCAR-CACO3
      CA=CA-CACO3
      IF(ABS(DOSE-DOS)-0.005*DOSE) 600,600,510
  510 DOS=DOSE
      GO TO 100
  600 MGOH2=AMG-EMG/((YOH*OH)**2)
      IF(MGOH2) 610,610,611
  610 MGOH2=0.0
  611 MG=AMG-MGOH2
      MGOH2=MGOH2+COLMG
      CO3=AL7*CAR
      IF(PH-9.75) 901,902,902
  901 CKSP=10.0**(-6.7+(PH-9.0)*0.813/0.75)
      GO TO 903
  902 CKSP=1.3E-6
  903 IF(CKSP-CA*CO3) 900,900,910
  900 COLF=0.0
      GO TO 913
  910 UVW=CA+CO3
      XYZ=UVW**2
      COLF=0.5*(-UVW+SQRT(XYZ+4.0*(CKSP-CA*CO3)))
      IF (COLF-CACO3-COLCA) 911,911,912
  911 CACO3=CACO3+COLCA-COLF
      GO TO 913
  912 COLF=CACO3+COLCA
      CACO3=0.0
  913 CA=CA+COLF
      ALK=COLF+CO3*(1.0+1.0/(2.0*AL6))+AL4*ORTO*(1.0+0.5/AL3)+0.2*POLY
     1  +0.5*OH+0.5*AM3
      MGOH2=58310.0*MGOH2
      CACO3=100000.0*CACO3
      STPHO=167000.0*STPHO
      FEOH2=89851.0*FEOH2
      SLUDG=MGOH2+CACO3+STPHO+FEOH2
      SOLID=SLUDG+TSS
      SEPN=TSS1/SOLID
      DOSE=DOSE*2.26E6/ABC
      FESO4=FESO4*152000.0
      ALK=ALK*1.0E5
      TPHO=TPHO*30974.0
      ORTO=ORTO*30974.0
      CA=CA*40080.0
      MG=MG*24310.0
      AMO=AMO*14007.0
      SFM1=(SFM+MGOH2*40.3/58.3+FEOH2*149.7/179.7+CACO3+STPHO)*SEPN
      STPHO=STPHO*(30974.0/167000.0)
      SOC1=SOC*SEPN
      DFM=MURES/1.8E-5+6.2E4*(DN-AMO)/14007.0+CA+MG+8.0E3*OH
     1  +6.0E4*(COLF+CO3*(1.0+1.0/2.0/AL6))+96.0/152.0*FESO4+5.6E4*FE
     2  +87.0/30.974*TPHO+34.0
```

```
      SNBC1=SNBC*SEPN
      SON1=SON*SEPN
      SOP1=(SOP+STPHO)*SEPN
      SBOD1=SBOD*SEPN
      VSS1=VSS*SEPN
      RSGCC=2.0
      RSMGL=2.0E6
      Q2=QIN*(SOLID-TSS1)*RSMGL/(RSMGL*(SLDEN-TSS1)+TSS1*SLDEN)
      Q1=QIN-Q2*(1.0-SLDEN/RSMGL)
      RO2=1.0+SLDEN*(RSGCC-1.0)/RSMGL
      CONCN=SLDEN/SOLID
      SOC2=SOC*CONCN
      SNBC2=SNBC*CONCN
      SON2=SON*CONCN
      SOP2=(SOP+STPHO)*CONCN
      SFM2=SFM1*(CONCN/SEPN)
      SBOD2=SBOD*CONCN
      VSS2=VSS*CONCN
      TSS2=SLDEN
      SWPKG=Q2*RO2*8345.7/QIN
      SVPKG=Q2*1000.0/QIN
      WTLIM = DOSE*8.3457*QIN/2000.0
      CHEMC=WTLIM*COLIM/(10.0*QIN)
      WTFES=FESO4*8.3457*QIN/2000.0
      COAGC=WTFES*COFES/(10.0*QIN)
      QMAX=QIN*PKTAV
      NUMB=QMAX/30.0
      NUMB=NUMB+1
      QEACH=QMAX/NUMB
      XYZ=ALOG(QEACH)/2.303
      COSTE=EXP(1./(0.099485-0.005877*ALOG(QEACH)))/1000.
      COSTE=COSTE*1.05
      TCOST=COSTE*NUMB
      COLKG=COLAB/(2600.0*QIN)*(1.5+(NUMB**1.351)/14.96)
      NUMAV=QIN/QEACH
      NUMAV=NUMAV+1
      IF (QEACH-11.0) 679,679,680
  679 HPPER=14.0*QEACH/11.0
      GO TO 681
  680 HPPER=14.0+0.06*(QEACH-11.0)
  681 THP=HPPER*NUMAV
      PWRCO=THP*CKWH*24.0*0.746/(1000.0*QIN)
      WRITE(3,24)
      WRITE(3,21) Q1,SOC1,SNBC1,SON1,SOP1,SFM1,SBOD1,VSS1,TSS1,DOC,
     1  DNBC,DN,TPHO,DFM,ALK,DBOD,CA,MG,PH,AMO,ORTO
      WRITE(3,25)
      WRITE(3,21) Q2,SOC2,SNBC2,SON2,SOP2,SFM2,SBOD2,VSS2,TSS2,DOC,
     1  DNBC,DN,TPHO,DFM,ALK,DBOD,CA,MG,PH,AMO,ORTO
      WRITE (3,31) NUMB,COSTE,TCOST,DOSE,WTLIM,CHEMC,COLKG
      WRITE (3,32) FESO4,WTFES,COAGC,PWRCO,RO2,SWPKG,SVPKG
      NCASE=NCASE+1
      GO TO 998
  999 CALL EXIT
      END
```

P REMOVAL BY LIME ADDIT ON

CASE NO. 4

INPUT STREAM

Q	SOC	SNBC	SON	SOP	SFM	SBOD
250.0000	9.0450	4.0470	1.4940	0.0900	3.1740	10.0460
VSS	**TSS**	**DOC**	**DNBC**	**DN**	**DP**	**DFM**
21.5260	24.7000	12.5820	11.0000	21.0000	5.4170	500.0000
ALK	**DBOD**	**CA**	**MG**	**PH**	**AMO**	**ORTHO-P**
265.4700	2.9590	50.0000	25.0000	7.8500	0.0000	0.0000

PROCESS CHARACTERISTICS

TSS1	PH	SLDEN	COLIM	FCA	FMG	TEMP
25.0000	11.0000	300000.0002	20.0000	0.9800	0.0100	25.0000
CKWH	**COLAB**	**PKTAV**	**COFES**			
3.0000	8000.0000	3.0000	25.0000			

ORTHO-P NOT GIVEN.ASSUMED TO BE 0.9*DP.

AMMONIA NITROGEN NOT GIVEN.ASSUMED TO BE 0.8*DN

OUTPUT STREAM 1

Q	SOC	SNBC	SON	SOP	SFM	SBOD
249.6430	0.4275	0.1913	0.0706	0.2529	23.0604	0.4749
VSS	**TSS**	**DOC**	**DNBC**	**DN**	**DP**	**DFM**
1.0176	25.0000	12.5820	11.0000	21.0000	0.1568	468.5456
ALK	**DBOD**	**CA**	**MG**	**PH**	**AMO**	**ORTHO-P**
199.6510	2.9590	60.7238	0.2746	11.0000	16.8000	0.1412

OUTPUT STREAM 2

Q	SOC	SNBC	SON	SOP	SFM	SBOD
0.4198	5131.0344	2295.7762	847.5141	3035.0016	276725.4190	5698.8802
VSS	**TSS**	**DOC**	**DNBC**	**DN**	**DP**	**DFM**
12211.2379	300000.0002	12.5820	11.0000	21.0000	0.1568	468.5456
ALK	**DBOD**	**CA**	**MG**	**PH**	**AMO**	**ORTHO-P**
199.6510	2.9590	60.7238	0.2746	11.0000	16.8000	0.1412

COSTS•SIZING•AND WASTE

NO• OF UNITS = 26

CAP COST PER UNIT = 294.091 KDOLLARS

TOTAL CAP COST = 7646.373 KDOLLARS

LIME DOSE = 266.778 PPM

LIME USED PER DAY = 278.307 TONS

LIME COST = 2.226 CENTS PER KGAL

LABOR COST = 0.085 CENTS PER KGAL

COAGULANT DOSE = 0.000 PPM FESO4

FESO4 USED PER DAY = 0.000 TONS

FESO4 COST = 0.000 CENTS PER KGAL

POWER COST = 0.029 CENTS PER KGAL

SLUDGE SPECIFIC GRAVITY = 1.150 GMS PER CM3

SLUDGE WT PER KGAL TREATED = 16.119 LBS

SLUDGE VOLUME PER KGAL TREATED = 1.679 GAL

DEFINITION OF COMPUTER PROGRAM SYMBOLS

INPUT-OUTPUT*

Symbol	Definition
ALK	Alkalinity as $CaCO_3$ (mg/l)
AMØ	Ammonia nitrogen (mg/l as N)
ATDS	Dummy variable for incrementing TDS
CA	Calcium (mg/l as Ca)
CHEMC	Cost of lime per 1000 gallons treated (¢)
CØAGC	Cost of $FeSO_4$ per 1000 gallons treated (¢)
CØFES	Cost of $FeSO_4$ ($/ton)
CØLKG	Cost of labor per 1000 gallons treated (¢)
CØLIM	Cost of lime ($/ton)
CØLAB	Operators salary ($/yr) (260-day year)
CØSTE	Capital cost of each Densator unit
CKWH	Power cost (¢/kwh)
DBØD	Dissolved BOD (mg/l)
DFM	Dissolved fixed matter (mg/l)
DN	Dissolved nitrogen (mg/l N)
DNBC	Dissolved nonbiodegradable carbon (mg/l C)
DØC	Dissolved organic carbon (mg/l C)
DØSE	Lime dose (mg/l)
DP	Dissolved phosphorus (mg/l P)
FCA	Fraction CaO in lime
FESØ4	$FeSO_4$ dose (mg/l $FeSO_4$)

*Note: The measurement units given are those in which these quantities appear on input and output. They may be handled in other units internally in the program.

FMG	Fraction MgO in lime
MG	Magnesium (mg/l Mg)
NCASE	Case number
NUMB	Number of Densator units
ØRTØ	Ortho-phosphate (mg/l P)
PH	pH of influent
PHF	Final pH
PKTAV	Peak to average flow ratio
PWRCØ	Power cost per 1000 gallons treated (¢)
QIN	Input flow rate (mgd)
Q1	Clarifier effluent flow rate (mgd)
Q2	Sludge waste flow rate (mgd)
RØ2	Specific gravity of sludge stream (mg/l)
SBØD	Influent solid BOD (mg/l)
SBØD1	Solid BOD in effluent stream 1 (mg/l)
SBØD2	Solid BOD in effluent stream 2 (mg/l)
SFM	Solid fixed matter in influent (mg/l)
SFM1	Solid fixed matter in effluent stream 1 (mg/l)
SFM2	Solid fixed matter in effluent stream 2 (mg/l)
SNBC	Solid nonbiodegradable carbon in influent (mg/l C)
SNBC1	Solid nonbiodegradable carbon in effluent stream 1 (mg/l C)
SNBC2	Solid nonbiodegradable carbon in effluent stream 2 (mg/l C)
SØC	Solid organic carbon in influent (mg/l C)
SØC1	Solid organic carbon in effluent stream 1 (mg/l C)

SØC2	Solid organic carbon in effluent stream 2 (mg/l C)
SØN	Solid organic nitrogen in influent (mg/l N)
SØN1	Solid organic nitrogen in effluent stream 1 (mg/l N)
SØN2	Solid organic nitrogen in effluent stream 2 (mg/l N)
SØP	Solid organic phosphorus in influent (mg/l P)
SØP1	Solid organic phosphorus in effluent stream 1 (mg/l P)
SØP2	Solid organic phosphorus in effluent stream 2 (mg/l P)
SLDEN	Sludge stream solids (mg/l)
SVPKG	Sludge volume per 1000 gallons treated (gals)
SWPKG	Wet sludge weight per 1000 gallons treated (lbs)
TCØST	Total capital cost of Densators (thousands of dollars)
TC	Operating temperature (°C)
TSS	Suspended solids in influent stream (mg/l)
TSS1	Suspended solids in effluent stream 1 (mg/l)
TSS2	Suspended solids in effluent stream 2 (mg/l)
VSS	Volatile suspended solids in influent (mg/l)
VSS1	Volatile suspended solids in effluent stream 1 (mg/l)
VSS2	Volatile suspended solids in effluent stream 2 (mg/l)
WTFES	Weight $FeSO_4$ used per day (tons)
WTLIM	Weight lime used per day (tons)

INTERNAL*

AH	Hydrogen ion activity
AL1	Concentration ratio $H_2PO_4^-/H_3PO_4$
AL2	Concentration ratio $HPO_4^{2-}/H_2PO_4^-$
AL3	Concentration ratio PO_4^{3-}/HPO_4^-
AL4	Concentration ratio PO_4^-/Total O-phosphate
AL5	Concentration ratio HCO_3^-/H_2CO_3
AL6	Concentration ratio CO_3^{2-}/HCO_3^-
AL7	Concentration ratio CO_3^{2-}/Total carbonate
AL8	Concentration ratio NH_3/NH_4^+
AL9	Concentration ratio NH_4^+/Total ammonia N
ALKCØ	Alkalinity due to HCO_3^-, CO_3^{2-}
AM3	NH_3 concentration (moles/l)
AM4	NH_4^+ concentration (moles/l)
BCAR	Original value of carbonate
BMG	Original value of magnesium
CACØ3	$CaCO_3$ precipitate
CAR	Total carbonates (moles/l)
CKSP	Empirical K_{SP} for $CaCO_3$ $(moles/l)^2$
CØLCA	Influent $CaCO_3$ supersaturation (moles/l)

---

* Note: Those symbols for which no measurement units are given are either dimensionless, or appear in different units at various points in the program.

CØLF	Effluent $CaCO_3$ supersaturation
CØLMG	Influent $Mg(OH)_2$ supersaturation (moles/l)
CØNCN	Solids concentration factor
CØ3	CO_3^{2-} concentration (moles/l)
DIV	Concentration of divalent ions (moles/l)
ECACØ	K_{SP} for $CaCO_3$ $(moles/l)^2$
EH1C	Ionization constant for HCO_3^- (moles/l)
EH2C	Ionization constant for H_2CO_3 (moles/l)
EH1P	Ionization constant for HPO_4^{2-} (moles/l)
EH2P	Ionization constant for $H_2PO_4^-$ (moles/l)
EH3P	Ionization constant for H_3PO_4 (moles/l)
EH2Ø	Ionization constant for H_2O $(moles/l)^2$
EFE	Solubility product for $Fe(OH)_2$ $(moles/l)^3$
EMG	Solubility product for $Mg(OH)_2$ $(moles/l)^3$
ENH4	Ionization constant for NH_4^+ (moles/l)
FEØH2	$Fe(OH)_2$ precipitate
FE	Fe^{2+} concentration (moles/l)
H	H^+ concentration (moles/l)
HPPER	Horsepower per Densator unit
INT	INT = 1 for influent, INT = 2 for effluent
MGØH2	$Mg(OH)_2$ precipitate
MURES	Ionic strength due to initial SO_4^{2-}, Cl^-, NO_3^-, Na^+, K
MU	Total ionic strength
NUMAV	Average number of Densators in use
OH	OH^- concentration(moles/l)

PØH	Effluent potential acidity (moles/l)
PØH1	Influent potential acidity (moles/l)
PØLY	Poly-phosphate concentration
QMAX	Maximum anticipated flow (mgd)
QEACH	Capacity of each unit (mgd)
QRS	Dummy variable
RSGCC	Specific gravity of dry sludge solids (gm/cm^3)
RSMGL	Density of dry sludge solids (mg/l)
SEPN	Solids separation factor = $\left(\frac{\text{carryover total solids after clarifier}}{\text{initial total solids}}\right)=\frac{TSS2}{Solid}$
SØLID	Total solids in reaction zone (mg/l)
SØRTØ	Ortho-phosphate precipitate
STPHØ	Total phosphate precipitate
SLUDG	Total precipitate (mg/l)
TDS	Total dissolved solids
THP	Total horsepower for all Densators
TPHØ	Total phosphate in solution
TK	Temperature (°K)
TRIV	Concentration of trivalent ions (moles/l)
U	Square root of ionic strength
UNIV	Concentration of univalent ions (moles/l)
UVW	Dummy variable
XYZ	Dummy variable
YCA	Activity coefficient of Ca^{2+}
YFE	Activity coefficient of Fe^{2+}
YH	Activity coefficient of H^{+}

YHP	Activity coefficient of HPO_4^{2-}
YH2P	Activity coefficient of $H_2PO_4^-$
YHCØ3	Activity coefficient of HCO_3^-
YCØ3	Activity coefficient of CO_3^{2-}
YØH	Activity coefficient of OH^-
YNH4	Activity coefficient of NH_4^+
YMG	Activity coefficient of MG^{2+}
YPØ4	Activity coefficient of PO_4^{3-}

APPENDIX B

REFERENCES

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APPENDIX C

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